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THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 10°.[1]

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In an earlier paper,[2] it was stated that the "considerable deviation of osmotic from gas pressure in the vicinity of 0°, while the two were found to be in substantial agreement in the neighborhood of 20°, made it desirable to determine the pressures of both cane sugar and glucose solutions at several intermediate temperatures;" and that "the intervals which have been selected for this purpose are 5°, 10° and 15°." The work upon cane sugar solutions at 5° has already been described.[3] The present paper gives an account of the pressures which they were found to exert at 10°.

The measurements in the present series are undoubtedly the most accurate which have thus far been made, owing to certain improvements in the method which have almost wholly eliminated the dilution of the solutions while in the cells.

[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558 **38**, 175.

[2] THIS JOURNAL, **38**, 175.

[3] *Ibid.*, **38**, 175.

We have frequently referred[1] to this dilution of the cell contents—due,"*not to leakage*, but to the sucking in of water from the wall behind the membrane while the cell is being closed and opened"—as the most obstinate of all the large sources of error which have been encountered. In the case of cane sugar, the average loss in rotation while the solutions were in the cells was as follows: Series II,[2] 2.8 per cent; Series III,[3] 1.47 per cent; Series IV,[4] 1.28 per cent; while in the present series (V) there was loss in rotation in only eight of the twenty experiments. This loss, moreover, was in every instance small as compared with the pressures measured, as will be seen in the following tabular statement:

Pressure measured.	Correction for loss in rotation.
12.00 atmospheres	0.005 atmosphere.
17.09 "	0.005 "
19.73 "	0.025 "
22.22 "	0.06 "
24.97 "	0.09 "

The whole loss has been corrected as *inversion*, though a portion of it is undoubtedly due to dilution. The quantities in question are, however, so small that they do not materially affect the results, whether the whole error is ascribed, on the one hand, to inversion, or, on the other, to dilution; or a part to inversion, and the remainder to dilution.

It is also to be noted that the temperatures maintained in the present work are much more constant than in any former series of measurements.

The material employed was from the same supply as that used in former measurements, and the statements made in earlier papers regarding its purity need not be repeated.

It may be noticed that the rotation of solutions of equal weight-normal concentration are not always identical. This is due to differences in the temperatures at which the rotation was determined.

[1] THIS JOURNAL. **36**, 26 and 49; **37**, 325; **37**, 327; **38**, 178.
[2] *Ibid.*, **36**, 39.
[3] *Ibid.*, **37**, 457.
[4] *Ibid.*, **38**, 175.

Table I.

0.1 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 12°.8; (2) at conclusion of experiment, 12°.8; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.08 mm. Cell used, H. Resistance of membrane, 136,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.46; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.97. Time of setting up cell, 4 P.M., March 2, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 5.						
11.45 P.M.	10°.0	10°.9	147.12	2.42	2.31	0.11
March 6.						
10.30 A.M.	10°.0	10°.7	146.78	2.43	2.31	0.12
				2.43	2.31	0.12

Molecular osmotic pressure, 24.25.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.050.

Table II.

0.1 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 12°.8; (2) at conclusion of experiment, 12°.8; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.09 mm. Cell used, G. Resistance of membrane, 219,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.69. Time of setting up cell, 3.30 P.M., March 2, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 5.						
8.40 A.M.	10°.0	10°.3	136.68	2.43	2.31	0.12
11.15 P.M.	10°.0	10°.9	136.17	2.45	2.31	0.14
March 6.						
10.30 A.M.	10°.0	10°.7	136.28	2.44	2.31	0.13
				2.44	2.31	0.13

Molecular osmotic pressure, 24.40.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.056.

Table III.

0.2 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 25°.0; (2) at conclusion of experiment, 25°.0; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.09 mm. Cell used, G. Resistance of membrane, 283,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.56; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02 Initial pressure, 4.66. Time of setting up cell, 11.30 A.M., January 21, 1908.

Time.	Temperature. Solution.	Manometer.	Volume N_2.	Pressure. Osmotic.	Gas.	Difference.
Jan. 22.						
11.40 A.M.	10°.2	10°.8	82.91	4.80	4.62	0.18
8.10 P.M.	10°.0	10°.9	82.87	4.80	4.62	0.18
Jan. 23.						
10.00 A.M.	10°.0	10°.7	82.37	4.83	4.62	0.21
				4.81	4.62	0.19

Molecular osmotic pressure, 24.05.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.041.

Table IV.

0.2 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 25°.0; (2) at conclusion of experiment, 25°.0; loss, 0°. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.14 mm. Cell used, D. Resistance of membrane, 141,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.78. Time of setting up cell, 11.30 A.M., January 21, 1908.

Time.	Temperature. Solution.	Manometer.	Volume N_2.	Pressure. Osmotic.	Gas.	Difference.
Jan. 22.						
11.40 A.M.	10°.2	10°.8	76.98	4.82	4.62	0.20
8.10 P.M.	10°.0	10°.9	76.98	4.82	4.62	0.20
10.30 P.M.	10°.0	10°.8	76.84	4.83	4.62	0.21
Jan. 23.						
10.00 A.M.	10°.0	10°.7	76.62	4.85	4.62	0.23
				4.83	4.62	0.21

Molecular osmotic pressure, 24.15.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.045.

Table V.

0.3 wt. normal solution, Experiment No. 1. *Rotation:* (1) original, 36°.6; (2) at conclusion of experiment, 36°.6; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.02 mm. Cell used, G. Resistance of membrane, 158,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.00. Time of setting up cell, 5.00 P.M., March 12, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
March 13.						
10.30 P.M.	10°.0	10°.6	53.40	7.20	6.92	0.28
March 14.						
8.45 P.M.	10°.0	10°.7	53.16	7.24	6.92	0.32
March 15.						
10.00 A.M.	10°.0	10°.8	53.44	7.21	6.92	0.29
				7.22	6.92	0.30

Molecular osmotic pressure, 24.07.
Molecular gas pressure, 23.07.
Ratio of osmotic to gas pressure, 1.043.

Table VI.

0.3 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 36°.7; (2) at conclusion of experiment, 36°.7; loss, 0.°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.08 mm. Cell used, O. Resistance of membrane, 112,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.36. Time of setting up cell, 4.00 P.M., March 17, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
March 19.						
5.00 P.M.	10°.00	10°.9	53.79	7.15	6.92	0.23
10.00 P.M.	10°.10	10°.9	53.86	7.14	6.93	0.21
March 20.						
8.30 A.M.	10°.10	10°.6	53.65	7.17	6.93	0.24
10.30 P.M.	10°.00	10°.8	53.73	7.15	6.92	0.23
				7.15	6.93	0.22

Molecular osmotic pressure, 23.83.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.032.

Table VII.

0.4 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 48°.1; (2) at conclusion of experiment, 48°.1; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.0 mm. Cell used, H. Resistance of membrane, 183,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.61. Time of setting up cell, 4 P.M., February 24, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 25.						
8.00 P.M.	10°.1	11°.2	40.86	9.53	9.24	0.29
Feb. 26.						
8.00 P.M.	10°.1	10°.6	40.98	9.52	9.24	0.28
10.00 P.M.	10°.0	10°.9	40.85	9.54	9.23	0.31
				9.53	9.24	0.29

Molecular osmotic pressure, 23.83.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.031.

Table VIII.

0.4 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 48°.1; (2) at conclusion of experiment, 48°.1; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.14 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.55. Time of setting up cell, 4.30 P.M., February 24, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 25.						
8.30 A.M.	10°.1	10.75	43.17	9.64	9.24	0.40
2.00 P.M.	10°.1	10.9	43.37	9.59	9.24	0.35
5.00 P.M.	10°.05	11.0	43.34	9.61	9.23	0.38
Feb. 26.						
10.00 P.M.	10°.00	10.9	43.38	9.61	9.23	0.38
				9.61	9.24	0.38

Molecular osmotic pressure, 24.03.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.040.

Table IX.

0.5 wt. normal solution. Experiment No. 1. *Rotatation:* (1) original, 59°.00; (2) at conclusion of experiment, 59°.00; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.03 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.9. Time of setting up cell, 3.30 P.M., February 20, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 21.						
9.00 A.M.	10°.0	10°.6	35.13	11.95	11.54	0.41
5.00 P.M.	10°.0	11°.0	35.11	11.96	11.54	0.42
Feb. 22.						
9.00 A.M.	10°.0	10°.4	35.15	11.94	11.54	0.40
4.00 P.M.	9°.9	10°.8	35.04	11.98	11.54	0.44
				11.96	11.54	0.42

Molecular osmotic pressure, 23.92.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.036.

Table X.

0.5 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 58°.7; (2) at conclusion of experiment, 58°.6; loss, 0°.1 = 0.17 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.64 mm. Cell used, G. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 3.88. Time of setting up cell, 4.00 P.M., March 17, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
March 18.						
10.00 P.M.	10°.0	10°.9	35.00	12.00	11.54	0.46
March 19.						
8.00 P.M.	10°.0	10°.8	34.87	12.04	11.54	0.50
March 20.						
10.30 A.M.	10°.0	10°.8	34.89	12.00	11.54	0.50
				12.01	11.54	0.49

Molecular osmotic pressure, 24.02.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.040.

Table XI.

0.6 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 69°.2; (2) at conclusion of experiment, 69°.2. loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.06 mm. Cell used, D. Resistance of membrane, 185,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.57. Time of setting up cell, 5.00 P.M., February 17, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 18.						
9.00 A.M.	10°.1	10°.4	29.10	14.50	13.85	0.65
5.00 P.M.	10°.1	10°.8	29.02	14.55	13.85	0.70
Feb. 19.						
2.00 P.M.	10°.1	10°.4	29.11	14.53	13.85	0.68
				14.53	13.85	0.68

Molecular osmotic pressure, 24.22.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.049.

Table XII.

0.6 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 69°.2; (2) at conclusion of experiment, 69°.2; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.03 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.8. Time of setting up cell, 5.00 P.M., February 17, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 18.						
9.00 A.M.	10°.1	10°.4	27.19	14.53	13.85	0.68
5.00 P.M.	10°.1	10°.8	27.11	14.57	13.85	0.72
Feb. 19.						
9.00 A.M.	10°.1	10°.5	27.20	14.53	13.85	0.68
2.00 P.M.	10°.1	10°.4	27.17	14.57	13.85	0.72
				14.55	13.85	0.70

Molecular osmotic pressure, 24.25.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.051.

Table XIII.

0.7 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 79°.3; (2) at conclusion of experiment, 79°.2; loss, 0°.1 = 0.13 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.16 mm. Cell used, G. Resistance of membrane, 373,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.38. Time of setting up cell, 4.00 P.M., January 24, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 25.						
11.00 A.M.	10°.1	10°.4	23.19	17.10	16.16	0.94
2.00 P.M.	10°.0	10°.7	23.18	17.11	16.16	0.95
5.00 P.M.	10°.0	10°.8	23.23	17.07	16.16	0.91
				17.09	16.16	0.93

Molecular osmotic pressure, 24.41.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.058.

Table XIV.

0.7 wt. normal solution. Experiment No 2. *Rotation:* (1) original, 79°.3; (2) at conclusion of experiment, 79°.3; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.17 mm. Cell used, D. Resistance of membrane, 187,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.63; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.93. Time of setting up cell, 4.00 P.M., January 24, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 25.						
11.00 A.M.	10°.1	10°.4	24.85	17.07	16.16	0.91
2.00 P.M.	10°.0	10°.7	24.84	17.08	16.16	0.92
5.00 P.M.	10°.0	10°.8	24.82	17.10	16.16	0.94
				17.08	16.16	0.92

Molecular osmotic pressure, 24.40.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.057.

Table XV.

0.8 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 89°.1; (2) at conclusion of experiment, 88°.9; loss, 0°.2 = 0.22 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.28 mm. Cell used, G. Resistance of membrane, 186,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.62; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.96. Time of setting up cell, 5.00 P.M., January 29, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Jan. 30.						
9.00 P.M.	9°.9	10°.8	20.17	19.70	18.46	1.24
Jan. 31.						
2.00 P.M.	10°.0	10°.6	20.14	19.73	18.47	1.26
4.00 P.M.	10°.0	10°.7	20.19	19.68	18.47	1.21
				19.70	18.47	1.23

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.63.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 89°.1; at conclusion of experiment, 89°.0; loss, 0°.1 = 0.11 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.25 mm. Cell used, D. Resistance of membrane, 184,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.64; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.46. Time of setting up cell, 5.00 P.M., January 29, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Jan. 30.						
2.00 P.M.	10°.0	10°.6	21.49	19.77	18.47	1.30
Jan. 31.						
2.00 P.M.	10°.0	10°.6	21.52	19.74	18.47	1.27
4.00 P.M.	10°.0	10°.7	21.52	19.75	18.47	1.28
				19.75	18.47	1.28

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.69.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.069.

Table XVII.

0.9 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 98°.4; (2) at conclusion of experiment, 98°.0; loss, 0°.4 = 0.41 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.88 mm. Cell used, D. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.62; (3) dilution, 0.06; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.94. Time of setting up cell, 4.00 P.M., February 14, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 15.						
1.00 P.M.	10°.0	11°.4	17.91	22.24	20.77	1.47
11.00 P.M.	10°.0	10°.6	17.93	22.22	20.77	1.45
Feb. 16.						
10.00 A.M.	10°.0	10°.4	17.93	22.20	20.77	1.43
				22.22	20.77	1.45

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.69.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.070.

Table XVIII.

0.9 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 98°.4; (2) at conclusion of experiment, 98°.0; loss, 0°.4 = 0.41 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.68 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.64; (3) dilution, 0.06; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.33. Time of setting up cell, 4.00 P.M., February 14, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 15.						
11.30 P.M.	10°.0	10°.6	19.18	22.22	20.77	1.45
Feb. 16.						
10.00 A.M.	10°.0	10°.4	19.15	22.21	20.77	1.44
				22.22	20.77	1.45

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.69.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.070.

Table XIX.

1.0 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 107°.4; (2) at conclusion of experiment, 106°.8; loss, 0°.6 = 0.56 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 1.29 mm. Cell used, D. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.64; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.89. Time of setting up cell, 5.00 P.M., February 11, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 12.						
8.00 P.M.	10°.3	11°.6	17.04	24.95	23.11	1.84
Feb. 13.						
9.00 A.M.	10°.2	10°.5	17.00	25.03	23.10	1.93
2.00 P.M.	10°.0	10°.9	17.03	24.98	23.08	1.90
				24.99	23.10	1.89

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.99.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.081.

Table XX.

1.0 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 107°.4; (2) at conclusion of experiment, 106°.8; loss, 0°.6 = 0.56 per cent. *Manometer:* No. 8; volume of nitrogen, 473.36; displacement, 0.85 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.66; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.24. Time of setting up cell, 5.00 P.M., February 11, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 12.						
11.30 P.M.	10°.2	10°.4	18.67	24.94	23.10	1.84
Feb. 13.						
9.00 A.M.	10°.2	10°.5	18.66	24.95	23.10	1.85
2.00 P.M.	10°.0	10°.9	18.68	24.92	23.08	1.84
				24.94	23.09	1.85

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.94.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.080.

Table XXI.—Summary of Results.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	10°.0	0°.0	0.00	2.43	2.31	0.12	24.25	23.10	1.050
0.1	10°.0	0°.0	0.00	2.44	2.31	0.13	24.40	23.10	1.056
0.2	10°.0	0°.0	0.00	4.81	4.62	0.19	24.05	23.10	1.041
0.2	10°.0	0°.0	0.00	4.83	4.62	0.21	24.15	23.10	1.045
0.3	10°.0	0°.0	0.00	7.22	6.92	0.30	24.07	23.07	1.043
0.3	10°.1	0°.0	0.00	7.15	6.93	0.22	23.83	23.08	1.032
0.4	10°.1	0°.0	0.00	9.53	9.24	0.29	23.83	23.10	1.031
0.4	10°.1	0°.0	0.00	9.61	9.24	0.37	24.03	23.10	1.040
0.5	10°.0	0°.0	0.00	11.96	11.54	0.42	23.92	23.08	1.036
0.5	10°.0	0°.1	0.01	12.01	11.54	0.49	24.01	23.09	1.042
0.6	10°.1	0°.0	0.00	14.53	13.85	0.68	24.22	23.09	1.049
0.6	10°.1	0°.0	0.00	14.55	13.85	0.70	24.25	23.09	1.051
0.7	10°.0	0°.1	0.01	17.09	16.16	0.93	24.41	23.09	1.058
0.7	10°.0	0°.0	0.00	17.08	16.16	0.92	24.40	23.09	1.057
0.8	10°.0	0°.2	0.03	19.70	18.47	1.23	24.63	23.09	1.067
0.8	10°.0	0°.1	0.02	19.75	18.47	1.28	24.69	23.09	1.069
0.9	10°.0	0°.4	0.06	22.22	20.77	1.45	24.69	23.08	1.070
0.9	10°.0	0°.4	0.06	22.22	20.77	1.45	24.69	23.08	1.070
1.0	10°.1	0°.6	0.09	24.99	23.10	1.89	24.99	23.10	1.081
1.0	10°.1	0°.6	0.09	24.94	23.08	1.85	24.94	23.09	1.080

Table XXII.—Summary of Results. Mean Values.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure	Difference.
0.1	10°.0	0°.0	0.0	2.44	2.31	0.13
0.2	10°.0	0°.0	0.0	4.82	4.62	0.20
0.3	10°.1	0°.0	0.0	7.19	6.93	0.26
0.4	10°.1	0°.0	0.0	9.57	9.24	0.33
0.5	10°.0	0°.05	0.005	12.00	11.54	0.46
0.6	10°.0	0°.00	0.00	14.54	13.85	0.69
0.7	10°.0	0°.05	0.005	17.09	16.16	0.93
0.8	10°.0	0°.15	0.025	19.73	18.47	1.26
0.9	10°.0	0°.40	0.06	22.22	20.77	1.45
1.0	10°.1	0°.60	0.09	24.97	23.09	1.87

Table XXII.—(Continued).

Concentration.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	24.33	23.10	1.053
0.2	24.10	23.10	1.043
0.3	23.95	23.08	1.038
0.4	23.93	23.10	1.036
0.5	23.97	23.09	1.039
0.6	24.24	23.09	1.050
0.7	24.41	23.09	1.058
0.8	24.66	23.09	1.068
0.9	24.69	23.08	1.070
1.0	24.97	23.10	1.081

It will be seen from Tables XXI. and XXII., which contain summaries of the results at 10°, that, at this temperature, the osmotic pressure of cane sugar solutions exhibits the same peculiarities that were observed at 0° and 5°, that is, an osmotic pressure which considerably exceeds the calculated gas pressure, and which diminishes slightly (relatively) from the 0.1 to the 0.4 weight-normal solution, and then increases with increasing concentration. If the pressures at 0°, 5° and 10° are compared, there is some evidence of a temperature coefficient to be discovered. This fact will be further commented upon when we present the results obtained at 15°.

JOHNS HOPKINS UNIVERSITY,
March 30, 1908.

[Contribution from the Chemical Laboratory of the University of Michigan.]

ON THE CONDENSATION OF NITROMALONIC ALDEHYDE WITH ACETONYLACETONE.

[FIRST PAPER.]

BY WILLIAM J. HALE AND CHARLES A. ROBERTSON.

In previous communications by Hill, Torrey, and others,[1] the work upon the condensation of nitromalonic aldehyde with acetone and its derivatives has been carefully described. The general mode of condensation has been found to be uniform

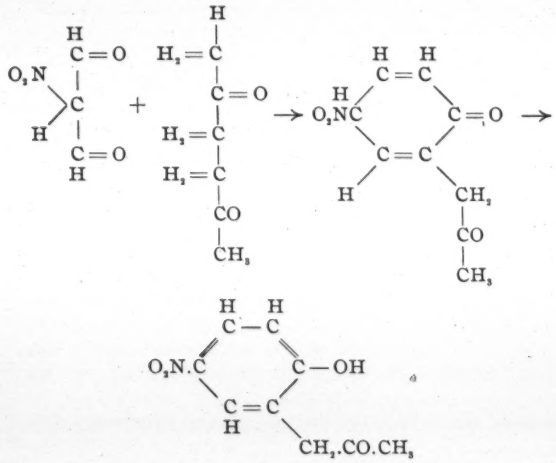
[1] THIS JOURNAL, **22**, 89 (1899); **24**, 1 (1900).

throughout and has always yielded the expected benzol derivatives, the constitution of which depended upon the substituents in the acetone molecule. The extension of this work to the diketones has seemed to us desirable. We have, accordingly, selected, in the first place, that ketone which would present two acetone nuclei, namely, acetonylacetone. In accordance with results from the earlier work (*loc. cit.*) we should expect to obtain from the condensation of this diketone with 2 molecules of nitromalonic aldehyde a dinitrodioxydiphenyl. In a contribution by Hill and one of us,[1] "On the Condensation of Nitromalonic Aldehyde with Benzylmethyl Ketone," it was shown that the production of a diphenyl derivative was attended with no difficulty whatsoever. We were led, therefore, to infer that in the condensation of 2 molecules of nitromalonic aldehyde with 1 molecule of acetonylacetone, a derivative of benzylmethyl ketone might possibly be first formed, but that as the result of a subsequent and final condensation this latter compound and the second molecule of nitromalonic aldehyde present would give the expected diphenyl derivative.

Into a reaction mixture containing two molecules of nitromalonic aldehyde and one of acetonylacetone, together with sodium hydroxide as a condensing agent, a current of carbon dioxide was passed in order to precipitate any of the nitrophenol that might in this way have been formed. A small amount of a yellow substance was readily thrown down. Its examinations clearly showed that we had to deal with a derivative of benzylmethyl ketone, a 2-acetonyl-4-nitrophenol, and that the condensation, therefore, had been, to a slight extent, at least, arrested at its middle stage. From the mother liquors, by acidification with hydrochloric acid, a large quantity of a light, yellow, crystalline substance was obtained. An examination proved that this was not the dinitrodioxydiphenyl we had anticipated, but a compound of an entirely different constitution. As it is the result of a new condensation, its description and study will be reserved for a second paper. From the facts just stated, we conclude

[1] THIS JOURNAL, **33**, 1 (1905).

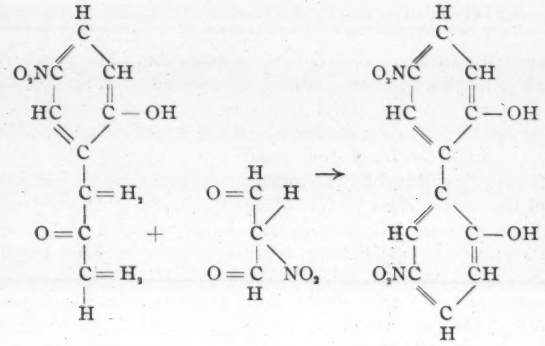
that the first stage in this condensation must consist in the union of one molecule of nitromalonic aldehyde with one molecule of acetonylacetone to give a 1-nitro-3-acetonyl-4-keto-Δ-2,5-dihydro-benzol, which passes over at once, upon acidification, into the 2-acetonyl-4-nitrophenol. Experiments have shown that the second molecule of nitromalonic aldehyde, under the conditions to be described later, does not enter into the reaction, and the same quantity of acetonyl-nitrophenol, as well of the light-yellow product from the mother liquor, may be obtained from the use of but one molecule of the aldehyde. We have then to deal with the simple reaction between one molecule of the aldehyde and one molecule of ketone:



The absence of any derivative of diphenyl in the reaction mixture is strongly indicative of the retarding influence which the substituent groups in the phenyl ring of the acetonyl-nitrophenol exert upon the further condensation between aldehyde and ketone.

Acetonylnitrophenol is a colorless, crystalline compound when pure. The sodium salt crystallizes in orange-red prisms changing to deep crimson upon dehydration. The action of alkyl haloids upon the sodium salts served as a method for obtaining the monoalkyl ethers of the compound and also for establishing the presence of but one hydroxyl group. The presence of the free ketone group in the acetonyl side chain is easily confirmed by the formation of an oxime. Oxidation of the methyl ether of this phenol by means of chromic acid gives the methyl ether of 5-nitrosalicylic acid and establishes, therefore, the constitution assigned. The compound undergoes nitration with ease, giving a 2-acetonyl-4,6-dinitrophenol with properties quite similar to the original mononitroderivative. The presence of an acetonyl group as a side chain in this compound leads at once to the inference that a second condensation with a molecule of nitromalonic aldehyde is possible under the proper conditions. To overcome the strongly negative character of the nitrophenolic group, its conversion into the form of an alkyl ether was found to suffice. The variation in the chemical constitution between a free phenol and its alkyl ether on the one hand, and that of its metallic salt on the other, may offer an explanation for the change in character of the phenyl group under these conditions. When the ethyl ether of acetonylnitrophenol condenses with one molecule of nitromalonic aldehyde in slightly alkaline solution, the reaction runs quite smoothly to the formation of a monoethyl ether of dinitrodioxydiphenyl, which can be easily precipitated with hydrochloric acid. In order to make possible the condensation of the free substance—the 2-acetonyl-4-nitrophenol—with one molecule of nitromalonic aldehyde, it was found necessary to alter the general method in use, by the employment of a large excess of alkali as the condensing agent. The excess of alkali may be considered to drive back the dissociation of the hydroxyl group and thus to lessen the strongly negative character of the entire phenyl ring.

[1] Baly, Edwards, and Stewart: J. Chem. Soc., **89**, 514 (1906).



In this case a derivative of a phenyldihydrobenzol may be regarded as the intermediate product, but upon acidification it passes rapidly into a 3,3′-dinitro-6,6′-dioxydiphenyl. A few of the derivatives of the several condensation products, sufficient to establish the constitution of all the compounds concerned and to indicate the general nature of these condensations, will be described.

Experimental Part.

Acetonylacetone was prepared by the method of Knorr,[1] and sodium nitromalonic aldehyde according to the directions of Hill and Torrey.[2]

2-Acetonyl-4-nitrophenol, $(CH_3.CO.CH_2)C_6H_3(NO_2)(OH)$.—One molecule of sodium nitromalonic aldehyde and slightly more than 1 molecule of acetonylacetone (1½ molecules are found quite sufficient) are dissolved in water with the addition of ⅛ molecule of sodium hydroxide. The strength of the alkaline solution should not exceed N/10, and the temperature of the mixture should not be allowed to rise over that of a low room-temperature. The slight excess of acetonylacetone insures the complete combination of all the aldehyde with the ketone and thus prevents any possibility of the formation

[1] Ber. d. chem. Ges., **22**, 2100 (1889).
[2] This Journal, **22**, 25 (1899).

of trinitrobenzol upon acidification of the reaction mixture, a possible result in the acidification of sodium nitromalonic aldehyde.[1] The amount of the alkali used is small, owing to the tendency for the second condensation already mentioned to take place. The presence of less than $^1/_8$ molecule of sodium hydroxide has been found not only to retard the progress of condensation but also to interfere materially with the precipitation of the free acetonylnitrophenol by carbon dioxide, other condensation products being simultaneously precipitated. In practice, 8 grams of sodium nitromalonic aldehyde are dissolved in 100 cc. of water, and to this solution 6.8 grams of acetonylacetone and 0.2 gram of sodium hydroxide are added. The color of the liquid soon becomes a deep red and after the lapse of 48 hours the condensation may be assumed to be complete. The solution is now diluted with water to twice its volume, in order to prevent a separation of the sodium salts of the products formed, and then treated with a rapid current of carbon dioxide to the point of saturation, when all of the acetonylnitrophenol will be precipitated in small, light-yellow crystals. The yield, however, is very poor, 1.7 grams, amounting to not more than 17 per cent of the theoretical quantity. This low yield is due, of course, to the formation of the new product now under investigation, about 65 per cent of the theoretical quantity being formed under the above conditions. The relative amounts of this new substance and of the acetonylnitrophenol remain practically the same under most conditions, approximating a ratio of 4:1 and changing only when the conditions are such as to involve the acetonylnitrophenol in secondary reactions. The use of piperidine as a condensing agent has been found to give good results. The same proportions and degree of dilutions as in the previous method are employed, excepting that a few drops of piperidine replace the sodium hydroxide. In a very short time the solution takes on a red color and gives after 48 hours about the same relative amounts of condensation products as in the former case. The crude product is most conveniently purified by several crystallizations from glacial

[1] This Journal, **22**, 98 (1899).

acetic acid. 2-Acetonyl-4-nitrophenol is readily soluble in acetone; fairly soluble in carbon disulphide, hot alcohol, or hot chloroform; from the two latter it may be crystallized. It is only sparingly soluble in benzol or carbon tetrachloride, and insoluble in ether, ligroin, or water, though boiling water dissolves it to a slight extent and deposits it again upon cooling in long, slender needles. From its solution in hot glacial acetic acid it crystallizes in beautiful, thin, colorless prisms which melt at 188.5° (corr.).

I. 0.1600 gram substance gave 0.3242 gram CO_2 and 0.0702 gram H_2O.

II. 0.2048 gram substance gave 13.7 cc. moist N at 20° and 734 mm. pressure.

	Calculated for $C_9H_9O_4N$.	Found. I.	II.
C	55.42	55.27	...
H	4.65	4.90	...
N	7.20	...	7.35

The Sodium Salt of 2-Acetonyl-4-nitrophenol.—When the free phenol is dissolved in water with just sufficient sodium hydroxide to effect neutralization, the sodium salt of the acetonylnitrophenol will separate, upon sufficient concentration, in small hexagonal plates of a bright-yellow color. This salt crystallizes well with 2 molecules of water of crystallization. A great part of this water of crystallization is lost over sulphuric acid, but the dehydration is not complete till 125°, the salt in the meantime having passed from a bright-yellow to the dark-red color of the anhydrous salt.

I. 0.6750 gram air-dried salt lost, at 125°, 0.0958 gram H_2O.

II. 0.1960 gram air-dried salt gave 0.0552 gram Na_2SO_4.

	Calculated for $C_9H_8O_4NNa.2H_2O$.	Found. I.	II.
H_2O	14.22	14.19	...
Na	9.10	...	9.13

2-Acetonyl-4-nitrophenol Methyl Ether, $(CH_3.CO.CH_2)C_6H_3(NO_2)(OCH_3)$.—The methyl ether is readily prepared by the action of methyl iodide upon the sodium

salt of the acetonylnitrophenol in alcoholic solution. After several hours' boiling on the water bath, under a reflux condenser, the clear solution is evaporated to dryness and the mass extracted with ether. Upon recrystallization from ether by the addition of low-boiling ligroin, the pure product melting at 60° (corr.) was obtained. The methyl ether is readily soluble in benzol, ether, acetone, chloroform, carbon tetrachloride, or alcohol; fairly soluble in hot ligroin, and insoluble in water. It is but sparingly soluble in low-boiling ligroin.

I. 0.1196 gram substance gave 0.2510 gram CO_2 and 0.0580 gram H_2O.

II. 0.2687 gram substance gave 17.2 cc. moist N at 23.6° and 735.4 mm. pressure.

	Calculated for $C_{10}H_{11}O_4N$.	Found. I.	II.
C	57.40	57.24	...
H	5.30	5.42	...
N	6.71	...	6.92

2-Acetonyl-4-nitrophenol Ethyl Ether, $(CH_3.CO.CH_2)C_6H_3(NO_2)(OC_2H_5)$.—The ethyl ether may be prepared by the action of ethyl iodide upon the sodium salt in a manner exactly similar to the preparation of the methyl ether. The solubilities of the ethyl ether are, in almost all respects, identical with those of the methyl ether, except that it is less markedly soluble in low-boiling ligroin. From its solution in ether, colorless prisms separate upon the addition of ligroin. They have a melting point of 70.5° (corr.).

I. 0.1456 gram substance gave 0.3150 gram CO_2 and 0.0794 gram H_2O.

II. 0.2478 gram substance gave 14.5 cc. moist N at 22° and 738 mm. pressure.

	Calculated for $C_{11}H_{13}O_4N$.	Found. I.	II.
C	59.16	59.00	...
H	5.87	6.10	...
N	6.29	...	6.40

Oxidation of 2-Acetonyl-4-nitrophenol Methyl Ether.—In order to establish conclusively the relative position of the acetonyl group in acetonylnitrophenol, the oxidation of the

methyl ether was attempted. Two grams of methyl ether were treated with a 4 per cent solution of potassium permanganate containing slightly more than the calculated quantity (5 molecules) of the salt. After 5-10 minutes' boiling, the excess of permanganate was decomposed by the addition of a few drops of alcohol, and the manganese dioxide filtered off. The clear filtrate was now acidified with hydrochloric acid and extracted with ether. The ether extract yielded a white product which melted at 148°-150°. This product showed all the properties of 5-nitrosalicylic acid methyl ether (m. p. 148°-149°). The result, therefore, establishes the constitution already assigned, by showing the acetonyl group is in the ortho position to the hydroxyl group in the original compound.

Oxime of 2-Acetonyl-4-nitrophenol Ethyl Ether, $(CH_3.C:NOH.CH_2)C_6H_3(NO_2)(OC_2H_5)$.—The oxime may be easily prepared by adding an alcoholic solution of acetonylnitrophenol ethyl ether to a concentrated aqueous solution of hydroxylamine hydrochlorate neutralized with a potassium carbonate solution. The oxime is precipitated in a short time. The product crystallizes out of alcohol in beautiful, colorless needles melting at 146° (corr.). It is extremely soluble in acetone, ethyl acetate, or chloroform; fairly soluble in hot benzol or alcohol, and nearly insoluble in ligroin or water. The formation of the oxime confirms the presence of the carbonyl, and hence the acetonyl, group in the original compound.

I. 0.1148 gram substance gave 0.2326 gram CO_2 and 0.0626 gram H_2O.

II. 0.1692 gram substance gave 18.4 cc. moist N at 23.5° and 748 mm. pressure.

	Calculated for $C_{11}H_{14}O_4N_2$.	Found. I.	II.
C	55.43	55.27	...
H	5.91	6.12	...
N	11.79	...	11.97

2-Acetonyl-4,6-dinitrophenol, $(CH_3.CO.CH_2)C_6H_2(NO_2)_2(OH)$.—Two grams of acetonylnitrophenol were dissolved in 40 grams glacial acetic acid with the

aid of gentle warming. Four grams of nitric acid (sp. gr. 1.40) were now added and the gentle warming continued for a few minutes only. The clear liquid must be cooled quickly and diluted with an equal volume of water, when the crystalline plates of the acetonyldinitrophenol soon make their appearance. This product may be easily crystallized out of glacial acetic acid, in which, however, it is quite soluble even in the cold. It is readily soluble in hot benzol or hot alcohol, in chloroform, acetone, or ethyl acetate; it is fairly soluble in ether or carbon disulphide, and but sparingly soluble in ligroin. In water it is slightly more soluble than the mononitro derivative. From its solution in hot benzol, beautiful glistening laminae which melt at 121° (corr.) separate upon the addition of ligroin.

I. 0.1098 gram substance gave 0.1803 gram CO_2 and 0.0368 gram H_2O.

II. 0.1602 gram substance gave 17.4 cc. moist N at 24.5° and 742 mm. pressure.

	Calculated for $C_9H_8N_2O_6$.	Found. I.	II.
C	44.96	44.77	...
H	3.35	3.75	...
N	11.69	...	11.80

2-Acetonyl-4,6-dinitrophenol Ethyl Ether, $(CH_3.CO.CH_2)C_6H_2(NO_2)_2(OC_2H_5)$.—The sodium salt of 2-acetonyl-4,6-dinitrophenol may be prepared in a manner exactly analogous to that for the sodium salt of the mononitrophenol, to which this salt bears also a close resemblance. The dried sodium salt is treated with ethyl iodide, using ethyl alcohol as a diluent and solvent, in the same manner as described for the preparation of an ether of the mononitro derivative. The ether extract gives a good yield of the product. This may be purified by crystallization from ligroin from which it separates in small, colorless prisms melting at 118.5° (corr.). The ethyl ether of acetonyldinitrophenol is readily soluble in acetone or ethyl acetate; fairly soluble in chloroform, benzol, or ether; and insoluble in ligroin and water.

I. 0.1304 gram substance gave 0.2348 gram CO_2 and 0.0564 gram H_2O.

II. 0.1600 gram substance gave 15.5 cc. moist N at 20.5° and 732.4 mm. pressure.

	Calculated for $C_{11}H_{12}O_6N_2$.	Found. I.	II.
C	49.22	49.12	...
H	4.51	4.84	...
N	10.47	...	10.59

3,3'-Dinitro-6,6'-dioxydiphenyl, $(HO)(NO_2)C_6H_3.C_6H_3(NO_2)(OH)$.—The presence of the acetonyl group in the compounds just described indicated at once the possibility of further condensation with nitromalonic aldehyde. As has already been mentioned, the presence of a second molecule of nitromalonic aldehyde in the preparation of acetonylnitrophenol did not in itself afford the condition for this further condensation. The use, however, of a large excess of alkali was found to have the desired effect, and under its influence, acetonylnitrophenol readily underwent the second condensation with the aldehyde. Two grams (1 molecule) of acetonylnitrophenol, together with 1.7 grams (slightly more than 1 molecule) of sodium nitromalonic aldehyde, were brought into solution in 40 cc. of water with the aid of 2 grams (5 molecules) of sodium hydroxide, giving an exactly normal solution of free alkali, *i. e.*, in excess of that required for neutralization. After standing 2 to 3 days at room temperatures, the liquid, in which a deep red color had developed, was diluted with 200 to 300 cc. of water and treated with a current of carbon dioxide. As no appreciable precipitate was formed, the absence of any unchanged acetonylnitrophenol was assured and the clear red solution was acidified with hydrochloric acid, the dinitrodioxydiphenyl being precipitated in a white, flocculent form. The yield was approximately 75 per cent of the theoretical. Dinitrodioxydiphenyl may be precipitated from its neutral or slightly alkaline solutions by means of carbon dioxide, but the presence of more than a very slight amount of alkali prevents this precipitation in dilute solutions. Under these conditions acetonylnitro-

phenol, if present, will be precipitated and may consequently be removed. The product may be advantageously crystallized from its solution in acetone to which a little ligroin is afterward added. The crystals appear in small colorless needles, and melt, when pure, at 301° (corr.). This dinitrodioxydiphenyl is readily soluble in alcohol, ethyl acetate, hot acetone, or hot glacial acetic acid. It is only sparingly soluble in ether, chloroform, or hot water, and practically insoluble in benzol, ligroin, or carbon disulphide.

I. 0.1268 gram substance gave 0.2420 gram CO_2 and 0.0376 gram H_2O.

II. 0.2088 gram substance gave 19.8 cc. moist N at 22° and 740.3 mm. pressure.

	Calculated for $C_{12}H_8N_2O_6$.	Found. I.	II.
C	52.16	52.05	...
H	2.92	3.31	...
N	10.17	...	10.41

A compound of this type but not of this constitution has been described by Kunze.[1] It is a dinitro derivative of paradiphenol obtained by nitration of the latter, whereas the substance we describe is derived from orthodiphenol. The properties of the two compounds are, as might be expected, somewhat similar. Another nitrodiphenol has been obtained by the action of potassium permanganate upon orthonitrophenol.[2] Its constitution, however, has not been determined. Presumably, the hydroxyl groups are not in the ortho position. A single experiment in which the action of potassium permanganate upon paranitrophenol was carried out as Goldstein directs for the orthonitrophenol did not give our dinitrodioxydiphenyl, which would have been formed if the oxidation and condensation had taken place at the ortho position to the hydroxyl group. The preparation of 3,3′-dinitro-6, 6′-dioxydiphenyl was indeed the primary object of this investigation. Its preparation has resulted from the synthesis of each benzol molecule in order, but the simultaneous syn-

[1] Ber. d. chem. Ges., **21**, 3331 (1888).
[2] Goldstein: J. Russ. Chem. Soc., **6**, 193 (1874).

thesis of the two benzol rings, as anticipated, might have been possible if we had not been dealing with strongly negative substituents. In this case further condensation can be effected only by the use of strong condensing agents, which, if employed at the first stage, would have resulted in the simultaneous condensation just mentioned. That we might further check the results of our work, a few derivatives of this dinitrodioxydiphenyl have been prepared. Owing to the small amount of material at our disposal, the salts of the diphenol were not studied. They may be prepared, however, by the usual methods. They dissolve readily in water, imparting a deep red color to the solution, a characteristic of this class of phenols.

3,3'-Diamino-6,6'-dioxydiphenyl, $(HO)(NH_2)C_6H_3.C_6H_3(NH_2)(OH)$.—The reduction of the dinitro derivative to the corresponding diamino form is easily accomplished by dissolving the former in warm, diluted alcohol and adding tin and concentrated hydrochloric acid. In the course of half an hour the reduction is complete and the clear solution, diluted with an equal volume of water, may be evaporated to small bulk over the steam bath to drive off the alcohol. After a further dilution of this residue with water, a current of hydrogen sulphide is passed through the hot liquid until all the tin is removed as sulphide. The clear filtrate gave, upon evaporation, long, colorless prisms of the hydrochlorate of this amino derivative. This hydrochlorate was transformed into the free body by bringing it into solution with water and just neutralizing with potassium carbonate solution, when the free diaminodioxydiphenyl is precipitated and may be filtered off at once. The yield is about 85 per cent of the theoretical. Diaminodioxydiphenyl is only sparingly soluble in hot alcohol and insoluble in almost all of the ordinary media. Its purification was therefore not attempted.

Oxidation of 3,3'-Diamino-6,6'-dioxydiphenyl to Diquinone, $C_6H_3O_2.C_6H_3O_2$.—Two and two-tenths grams (1 molecules) of the diamino derivative was dissolved in ten times its weight of diluted sulphuric acid (1 part acid to 3 parts water by weight). To this solution, 3.6 grams ($1^1/_4$ molecules)

sodium dichromate in 16 cc. of water were added, and the mixture warmed very gently. The glistening, yellow crystals of the diquinone separated almost immediately, and were filtered off and dried. The yield was about 60 per cent of the theoretical. Diquinone crystallizes best from glacial acetic acid in small prisms of a light-lemon color. It crystallizes also in fine, long prisms from ethyl acetate. The pure substance melts at 192° (corr.). Diquinone is extremely soluble in acetone; fairly soluble in benzol, chloroform, or alcohol; but slightly soluble in ether; and insoluble in ligroin. It dissolves sparingly in hot water from which it crystallizes on cooling.

0.1298 gram substance gave 0.3196 gram CO_2, and 0.0344 gram H_2O.

	Calculated for $C_{12}H_4O_4$.	Found.
C	67.28	67.14
H	2.82	2.96

This product is identical with the diquinone described by Barth and Schreder,[1] who, however, found a slightly lower melting point, 186-187° (uncorr.).

Reduction of Diquinone to Dihydroquinone, $(HO)_2C_6H_3.C_6H_3(OH)_2$.—When 2 grams of the diquinone were suspended in water, a current of sulphur dioxide led through the vessel for a half hour or more to complete saturation, and the vessel then stoppered and set aside for a few hours, the reduction of the diquinone was accomplished. From the clear solution, the dihydroquinone may be extracted with ether. The dihydroquinone thus obtained can be crystallized from a small quantity of water containing sulphur dioxide, which will prevent any possible reoxidation to the quinone. Several recrystallizations are necessary before a product of sufficient purity can be obtained. The pure product appears in the form of colorless prisms melting at 237°-238° (uncorr.) with decomposition. It is readily soluble in alcohol, acetone or ethyl acetate; fairly soluble in ether or hot water; slightly soluble in chloroform or benzol; and insoluble in ligroin.

[1] Monats. Chem., 5, 603 (1884).

This dihydroquinone is sweet to the taste; colored red in aqueous solution by ferric chloride; and in all other respects, identical with the dihydroquinone described by Barth and Schreder.[1] The identity of both the diquinone and dihydroquinone with those described by Barth and Schreder further serves to establish the constitution assigned to the condensation products just studied. The preparation of the dinitrodioxydiphenyl by the method described above affords also a simple means for the preparation of its monoalkyl ethers.

3,3'-Dinitro-6,6'-dioxydiphenyl Dimethyl Ether, $(CH_3O)(NO_2)C_6H_3.C_6H_3(NO_2)(OCH_3)$.—A small quantity of the dinitrodioxyphenyl was brought into solution in water in the form of a sodium salt with the aid of an excess of sodium hydroxide. To this strong alkaline solution was added a little dimethyl sulphate and the vessel well shaken, with warming. In a few minutes a white precipitate separates. This is removed by filtration and thoroughly digested with a warm solution of sodium carbonate in order to remove any unchanged diphenol. The crude product thus obtained is conveniently purified by crystallization from acetone and ligroin from which it separates in small needles melting at 264° (corr.). The dimethyl ether of dinitrodioxydiphenyl is readily soluble in warm acetone, chloroform, alcohol, or ethyl acetate, and fairly soluble in benzol. It is insoluble in ligroin or water.

I. 0.1382 gram substance gave 0.2788 gram CO_2 and 0.0516 gram H_2O.

II. 0.2428 gram substance gave 20.9 cc. moist N at 22.4° and 736.4 mm. pressure.

	Calculated for $C_{14}H_{12}O_6N_2$.	Found. I.	II.
C	55.24	55.03	...
H	3.97	4.18	...
N	9.23	...	9.38

3,3'-Dinitro-6,6'-dioxydiphenyl Diethyl Ether, $(C_2H_5O)(NO_2)C_6H_3.C_6H_3(NO_2)OC_2H_5$.—The diethyl ether of dinitrodioxydiphenyl may be prepared by converting the

[1] Monats. Chem., 5, 600 (1884).

free diphenol into its sodium salt, dissolving the dried salt in ethyl alcohol to which ethyl iodide has been added, and boiling the solution for several hours under a reflux condenser over a water bath. The clear liquid thus obtained is evaporated to dryness and the mass extracted with ether, in which the diethyl ether is slowly taken up. Crystallization from acetone or from ethyl acetate gave needle clusters with a melting point of 271° (corr.). The diethyl ether is fairly soluble in warm acetone, alcohol, chloroform or ethyl acetate; only slightly soluble in ether or hot benzol; and insoluble in ligroin or water. It resembles very closely the dimethyl ether.

I. 0.1202 gram substance gave 0.2542 gram CO_2 and 0.0536 gram H_2O.

II. 0.2216 gram substance gave 17.5 cc. moist N at 23.8° and 741.4 mm. pressure.

	Calculated for $C_{18}H_{16}O_8N_2$.	Found. I.	II.
C	57.80	57.68	...
H	4.85	4.99	...
N	8.45	...	8.60

3,3'-Dinitro-6,6'-dioxydiphenyl Monoethyl Ether, $(HO)(NO_2)C_6H_4.C_6H_3(NO_2)OC_2H_5$.—The preparation of this ether is accomplished through the condensation of the ethyl ether of acetonylnitrophenol with nitromalonic aldehyde. The condensation is carried out by dissolving one molecule of acetonylnitrophenol ethyl ether in alcohol and adding the solution to one molecule of sodium nitromalonic aldehyde in a small quantity of water containing a little sodium hydroxide. The addition of more than one molecule of alkali, the amount required for the condensation of the free acetonylnitrophenol and sodium nitromalonic aldehyde, is not necessary. The operation requires from 2 to 3 days for its completion. The final red solution was extracted with ether, in order to remove any unchanged ethyl ether of acetonylnitrophenol and then acidified with hydrochloric acid, when a flocculent white precipitate of the monoethyl ether appeared. The yield was about 75 per cent of the theoretical. The monoethyl ether is very soluble in warm acetone, alcohol or ethyl acetate;

fairly soluble in warm chloroform or benzol; and insoluble in ligroin or water. It crystallizes from acetone in colorless, fine, silky needles which mat closely together. The melting point is 224° (corr.).

I. 0.1552 gram substance gave 0.3136 gram CO_2 and 0.0569 gram H_2O.

II. 0.2848 gram substance gave 24.1 cc. moist N at 20.8° and 738.7 mm. pressure.

	Calculated for $C_{14}H_{12}O_6N_2$.	Found. I.	II.
C	55.24	55.11	...
H	3.97	4.10	...
N	9.23	.....	9.32

The condensation of the alkylated acetonylnitrophenol with nitromalonic aldehyde requires but little alkali as a condensing agent. The use of a larger amount somewhat facilitates the reaction and hence its employment in the above case. The presence, therefore, of the ethoxyl group in the phenyl ring is seen to have a much smaller retarding action upon the further condensation of the acetonyl group than has the hydroxyl group in the same substituent. The condensations which are possible in the use of the diketone, acetonylacetone, have proved of much interest in the study of dialdehydes, and will, it is hoped, still further enlarge the possibilities of these ring formations when the constitution of the compound now under study is established and its formation explained. For the kind services of Mr. A. C. Houghton in aiding and furthering this work, we wish to express our appreciation and gratitude.

ANN ARBOR, MICHIGAN,
Nov. 1, 1907.

[Contributions from the Chemical Laboratory of Harvard College.]

ROSOCYANINE.

BY LATHAM CLARKE AND C. LORING JACKSON.

The reaction of turmeric paper with boric acid was observed,[1] and used as a test for this substance, even before the first

[1] Trommsdorff: Trommsdorff's J. v. Pharm., **18**, 96. Sementini: Bibliothèque Britannique, January, 1815.

attempt[1] to study curcumine, the yellow coloring matter of turmeric, but in spite of this early discovery, very little attention has been paid to the nature of this interesting reaction. So far as we can find, only two men have tried to study it. The first paper on this subject was by Schlumberger,[2] in which he described the preparation and properties of the substance formed by the action of boric acid and a strong acid on curcumine in alcoholic solution, and called it rosocyanine from its crimson rose color in solution and its blue salts. He stated that it contains no boron, and that on boiling it with alcohol, a resinous substance, called by him pseudocurcumine, was produced, from which he could obtain neither curcumine nor rosocyanine. Curcumine, when boiled with boric acid and alcohol, formed a vermilion product containing boric acid which was given up on boiling with water, leaving pseudocurcumine. This vermilion substance gave a purple color with alkalies, and rosocyanine with acids. His paper contains no analyses. Considering the very impure curcumine used by him, his results are surprisingly accurate; the few mistakes will be pointed out in the description of the similar experiments tried by us.

Six years later, Ivanow-Gajewski[3] took up the study of rosocyanine in connection with his research on curcumine. The meagre abstracts of his papers, which alone are accessible to us, state that he analyzed rosocyanine, but failed to establish any satisfactory formula for it, which is not surprising, as at that time he was working with a very impure curcumine melting at 140° (instead of 178^{04} or 183^{05}). The next year he stated[6] that rosocyanine contains no boron, and that, fused with potassic hydrate, it yields paraoxybenzoic acid. This last observation, if correct, is of no value in determining the constitution of rosocyanine, because our experiments show that it contains the unaltered vanillin group of curcumine.

[1] A. Vogel, Sr., and Pelletier: J. de. Pharm., **1**, 289.
[2] Bull. Soc. Chim. [2], **5**, 194 (1866).
[3] Ber. d. chem. Ges. **5**, 1103 (1872).
[4] Jackson and Menke: THIS JOURNAL, **4**, 77.
[5] Ciamician and Silber: Gazz. chim. ital., **27**, I, 561 (1897).
[6] Ber. d. chem. Ges., **6**, 196 (1873).

It is strange that this reaction has not attracted more attention, for it is certainly one of the most curious in organic chemistry, and is familiar to all chemists. How does the boric acid modify the molecule of curcumine? And why should boric acid alone[1] act in this way? We have made some progress toward answering these questions and have decided to publish our results now instead of waiting until we can give a more complete answer, because this cannot be done before the constitution of curcumine is determined, and owing to the unmanageable nature of its derivatives, like all others who have worked in this field we have found that the research advances with extreme slowness, so that it will be a long time before we can bring our work on rosocyanine to a conclusion.

The most obvious answer to the questions proposed above would be that the boric acid formed a compound with curcumine, and this supposition has been advanced by Ostwald in his "Scientific Foundations of Analytical Chemistry,"[2] but, as the only men who had worked with this substance, Schlumberger and Ivanow-Gajewsky, both had stated that it contains no boron, Ostwald's hypothesis, when proposed, was contrary to the observed facts, and as our experiments amply confirm these statements of our predecessors, it must be rejected.

The rosocyanine used by us was prepared from pure curcumine by heating it with boric acid and sulphuric acid in alcoholic solution. It was freed from mineral impurities by washing with water, from unaltered curcumine with ether, in which rosocyanine is insoluble. Although Schlumberger says he prepared it in fine needles, we have not yet succeeded in obtaining it in crystals, but it appears as a purple powder looking much like rosaniline except that the green metallic reflex has a yellower tinge. It decomposes without melting

[1] The coloration produced on turmeric paper by a solution of zirconic oxide in hydrochloric acid seems to be caused by something else than rosocyanine to judge from Brush's account of it [J. prakt. Chem., **62**, 7 (1854)]; and so far as we know it has not been proved that rosocyanine is formed by the action on turmeric paper of compounds of titanium, molybdenum, niobium, or tantalum. We hope to study these reactions later.

[2] M'Gowan's translation, p. 209 (1900).

between 200° and 230°, dissolves in alcohol, forming a crimson rose solution, free from even a trace of magenta, and forms salts of a pure and beautiful blue color.

The absence of boron was proved by a qualitative test, which was shown by special experiments to be delicate enough to detect the boron if it was present as an essential constituent, and also even more definitely by the combustions of rosocyanine, which gave the same percentages of carbon and hydrogen as those in curcumine. A molecular weight determination showed that it is an isomer, not a polymer, of curcumine, and its formula[1] is, therefore, $C_{14}H_{14}O_4$.

Only one salt of rosocyanine, $C_{14}H_{13}RO_4$, could be obtained with an alkali, whereas curcumine gives two, $C_{14}H_{13}RO_4$ and $C_{14}H_{12}R_2O_4$. It is evident, therefore, that one of the hydroxyl groups of the curcumine takes part in the formation of rosocyanine, and to determine which of the two it was, the monomethylcurcumine was prepared from the potassium salt made from potassic carbonate, so that in this case the more acid of the two hydroxyls was converted into a methoxyl. This monomethyl ether gave the rosocyanine reaction, as shown by the characteristic crimson color of the alcoholic solution of the product, but, as was expected, the monomethylrosocyanine formed no salts. As, however, the position of this more acid hydroxyl in curcumine had not been as yet determined, we oxidized the monomethylcurcumine, and obtained veratric acid, $C_6H_3(OCH_3)_2COOH$; this more acid hydroxyl, therefore, is attached to the benzene ring, in other words, is the vanillin hydroxyl, which is in harmony with the fact that salts of vanillin can be formed by the decomposition of carbonates. It follows from these experiments that the hydroxyl which takes part in the rosocyanine reaction is the less acid one on the side chain, the benzene nucleus probably taking no part in the reaction. This view was supported by the observations that the dimethyl ether of curcumine, $C_{14}H_{12}(CH_3)_2O_4$, gave no rosocyanine, and that

[1] We have proved (Ber. d. chem. Ges., **38,** 2712; **39,** 2269) that the formula of curcumine is $C_{14}H_{14}O_4$ and not the $C_{21}H_{20}O_6$ ascribed to it by Ciamician and Silber (Gazz. chim. ital., **27,** I, 561).

protocurcumine, $C_6H_3(OH)_2C_7H_7O_2$, gave the rosocyanine reaction.

The facts that rosocyanine forms one salt and curcumine two indicate that in rosocyanine the second curcumine hydroxyl has been modified in some way. This modification might consist in the conversion of the hydroxyl into (*a*) a less acid (more alcoholic) hydroxyl, (*b*) a keto or aldehyde group, or (*c*) an oxide. (*a*) Rosocyanine forms only a monacetic ester, $C_{14}H_{13}(C_2H_3O)O_4$, which indicates that it contains only one (the vanillin) hydroxyl, but this indication cannot be accepted definitely until the acet compounds of curcumine have been submitted to a revision,[1] because Menke and one of us[2] found that the usual product of the action of acetic anhydride and sodic acetate on curcumine was a viscous monacetcurcumine, only one preparation out of many, giving a crystallized diacetcurcumine melting at 154°, and Ciamician and Silber,[3] by the action of acetic anhydride, obtained a monacetcurcumine which they succeeded in crystallizing, when it melted at 170°-171°. As there is no doubt that curcumine contains two hydroxyls, these experiments seem to show that one of these may escape the action of the acetic anhydride, and it is possible, although improbable, that the same may be true of rosocyanine. (*b*) As hydroxylamine hydrochloride has no action on rosocyanine, no ketone or aldehyde can have been formed. (*c*) It follows, therefore, that the oxygen of the less acid (side chain) hydroxyl of the curcumine must have been converted into the oxide form, provided further experiments show that our reasoning in the case of the hydroxyl (*a*) is correct.

The dihydride of curcumine, $C_{14}H_{16}O_4$, gave no rosocyanine reaction. In this dihydride, the hydrogen is probably added to one of the double bonds, although we cannot yet give an experimental proof of this; in that case the double bond also takes part in the rosocyanine reaction.

If rosocyanine is allowed to stand with an aqueous solution

[1] A temporary lack of material compels us to postpone this revision to a later paper.

[2] This Journal, **6**, 77 (1884–5).

[3] Gazz. chim. ital., **27**, I, 561 (1897).

of potassic hydrate in the cold, in a short time it is converted back into curcumine. Under similar conditions the monomethylrosocyanine gives monomethylcurcumine.

It would not be hard to write a formula for rosocyanine based on the observations described above, but we think it wiser to postpone this until our further researches on curcumine have provided a safe experimental basis for such a formula, especially as it must also account for rubrocurcumine, which will be described presently.

In the hope of answering the question why only boric acid should give the rosocyanine reaction we have tried to isolate the intermediate products between curcumine and rosocyanine, and for this purpose have taken up the study of the red substance formed, according to Schlumberger,[1] by the action of boric acid and alcohol on curcumine. We soon found that there are two red products of this reaction, which Schlumberger could hardly have distinguished, as he made no analyses. The more stable is obtained by precipitation with water; it has a full vermilion color, is free from boron, and contains percentages of carbon and hydrogen corresponding to the formula $C_{14}H_{14}O_4$. That it is not a mixture of curcumine and rosocyanine (which also have this formula) is proved by its color, and especially by the facts that it is much more soluble in alcohol than either of these bodies, and gives an acet compound, $C_{14}H_{13}(C_2H_3O)O_4$, of an orange red color which crystallizes well and has a constant melting point of 245°. Acetcurcumine[2] melts at 170°-171°, diacetcurcumine[3] at 154°, and acetrosocyanine does not melt.

Rubrocurcumine, as we propose to name this substance, shows but a slight stability, passing back to curcumine on standing at ordinary temperatures for two weeks, while, on boiling with water, the same change takes place in a few minutes. Schlumberger, under these conditions, obtained his supposititious pseudocurcumine, which was probably curcumine mixed with a large amount of resinous impurity from the turmeric. Between 200° and 240°, the rubrocurcumine

[1] Bull. Soc. Chim. [2], **5**, 194 (1866).
[2] Ciamician and Silber: Gazz. chim. ital., **27**, I, 561 (1897).
[3] This Journal, **6**, 78 (1884–5).

is converted into rosocyanine, and the same change is produced very easily by warming it with dilute sulphuric acid. With an aqueous alkali, the rubrocurcumine gives a royal purple solution, but this quickly changes color, a salt of curcumine being apparently formed.

The other product of this reaction is obtained when the alcoholic solution of boric acid and curcumine, after the reaction has taken place, is precipitated with ether instead of water. It has a somewhat deeper red color than rubrocurcumine, but could hardly be distinguished from it by the eye alone. It seems to be an addition compound of boric acid and curcumine, but we have not yet brought it into a state fit for analysis. That it is not a mixture of boric acid with rubrocurcumine, rosocyanine, or curcumine is shown by the fact that on standing it is converted, in a short time, into a waxy mass, a property shown by none of those three compounds. Water decomposes it at once into rubrocurcumine and boric acid.

There is no doubt, we think, that this addition compound is formed at first in the preparation of rosocyanine from curcumine. Whether it is converted into rosocyanine directly, or into rubrocurcumine, which the sulphuric acid then changes to rosocyanine, cannot be decided with our present data. The intermediate formation of rubrocurcumine certainly seems probable, but we have no experimental proof that this action can be brought about by the reagents present—hot alcohol, sulphuric acid, and the small amount of water used to dilute it. Our next experiments in this line will deal with this subject, the establishment of the composition of the addition product and the determination of the constitution of curcumine, rosocyanine, and rubrocurcumine.

Some experiments on the preparation of rubrocurcumine and rosocyanine showed that the presence of water was unfavorable to both these reactions, and that rosocyanine can be formed when pure acetone or glacial acetic acid is substituted for the alcohol, so that this seems to act only as a solvent. Glacial acetic acid can also take the place of the sulphuric (or hydrochloric) acid, and it can be replaced also

by mannite or glycerine in the preparation of rosocyanine, although in these latter cases the effect of the strong acid is probably obtained from the boric acid, intensified by the polyatomic alcohol.

F. Emich, in a paper[1] contributed to the Lieben-Festschrift, makes the following statement: "Färbt man z. B. Schafwolle, Seide, oder Schiesswolle mit Curcumatinctur, so entsteht nach der Behandlung mit angesäuerter Boraxlösung wohl eine Roth- oder Braunfärbung beim Eintrocken, *aber keine Bläuung mit Soda* (höchstens eine dunklere Braunfärbung). Die Bläuung tritt nur auf, wenn man den Farbstoff auf Papier, Baumwolle, oder Leinenfaser niederschlägt. Es scheint sich also um eine Reaction der Cellulose zu handeln." This inference of Emich's, that the blue color is due to a reaction of cellulose, is disproved by our results, as we have repeatedly made rosocyanine and its blue salts under conditions where no cellulose was present, but in consideration of this definite statement of his, that the blue coloration is not obtained on wool, we have felt obliged to try the following experiment: A piece of white woolen cloth was dyed with an alcoholic solution of curcumine, and after drying, treated with a mixture of dilute sulphuric acid and boric acid. On drying at 100°, the wool took on a crimson color, which turned to a dark, vivid blue when treated with dilute sodic hydrate or ammonic hydrate. As we, therefore, found no difficulty whatever in obtaining the rosocyanine reaction on wool, we have not thought it worth while to repeat the experiment with silk or gun cotton.

EXPERIMENTAL.

Preparation of Rosocyanine.—After several experiments the following method of preparation proved the most convenient.

Four grams of sulphuric acid (specific gravity 1.84) were poured into 80 cc. of alcohol, and to the mixture, 4 grams of crystallized boric acid and 4 grams of curcumine (purified by crystallization from alcohol and melting at 178°) were added. The whole was then heated on the water bath in a flask with a return condenser, when, after a few seconds, the

[1] Ann. Chem. (Liebig), **351**, 429 (1907).

solution took on a deep crimson color, and all the curcumine and boric acid went into solution. After the heating had been continued for three or four hours, yellowish green metallic patches of nearly pure rosocyanine appeared adhering to the sides of the flask. The hot solution was then poured into 400 cc. of water, and the precipitate thus formed filtered out, washed with water till free from acid, and dried. This product was a fine greenish powder consisting essentially of a mixture of rosocyanine and unchanged curcumine. We tried at first to remove the curcumine by dissolving the product in alcohol and precipitating with ether, in which rosocyanine is insoluble, but the precipitate formed was so finely divided as to be unmanageable. Accordingly the crude product was extracted for six hours with ether, and then in order to remove any curcumine which was protected from solution by a coating of rosocyanine, the residue was dissolved in alcohol, and precipitated by pouring it into three to four times its volume of a two per cent solution of sodic chloride. If no salt was used in the water, the rosocyanine appeared in such a finely divided form that it was impossible to wash it. The new precipitate was washed thoroughly with water, dried, and extracted again with ether until it ceased to give a colored solution.

The rosocyanine obtained in this way was pure, as far as we could find. The yield was about 80 per cent of the weight of the curcumine. By using absolute instead of common alcohol, in some cases the yield was raised to 95 per cent, but we did not find this gain in yield sufficient to make up for the trouble of preparing absolute alcohol, and therefore used common alcohol in most of our preparations. The addition of water, on the other hand, diminished the yield, as with a mixture of equal parts of alcohol and water 60 per cent was the best we could obtain. Other modifications of the process also led to poorer results, although a certain amount of rosocyanine can be obtained under a great variety of conditions. Rosocyanine can be prepared to advantage from the viscous residues left by the evaporation of the alcoholic mother liquors from the purification of crude curcumine. Upon

treating this impure mass with alcohol, sulphuric acid, and boric acid, as described above, rosocyanine is formed, which is easily freed from the resinous impurity by washing with ether. Although rosocyanine can be converted into curcumine by standing with aqueous sodic hydrate, it is not practicable in this way to increase the yield of curcumine from turmeric, because this conversion is far from quantitative.

Composition of Rosocyanine.

Both Schlumberger[1] and Ivanow-Gajewsky[2] state that rosocyanine contains no boron, but, as we have seen no account of the experimental methods used by them, we thought it necessary to test our rosocyanine for boron as follows: A quantity of it was fused with a mixture of sodic carbonate and potassic nitrate until all the organic matter had been decomposed, the residue was then dissolved in water, acidified with hydrochloric acid, and tested for boric acid with turmeric paper, when the result was entirely negative.

To show that boric acid, if present, would have been detected by this method, 1 gram of rosocyanine was mixed with 0.05 gram of boric acid, and upon submitting it to the same treatment a strong test for boric acid was obtained. Also 0.2642 gram of boric acid mixed with about 0.6 gram of rosocyanine were fused with a mixture of 10 parts of sodic carbonate and 5 of potassic nitrate. The residue was dissolved in water, acidified with hydrochloric acid, and the excess of acid destroyed with a mixture of 4 parts of potassic iodide to one of potassic iodate, the liberated iodine removed by treatment with sodic thiosulphate, and the free boric acid titrated by the mannite method of L. C. Jones;[3] the amount found was 0.2508 gram instead of 0.2642 gram. This agreement between the weight of acid used and that recovered is as close as could be expected, since, owing to the danger of decomposing the boric acid, no very complete drying of the original amount was attempted. We have not studied the subject further, as

[1] Bull. Soc. Chim. [2], **5**, 194 (1866).
[2] Ber. d. chem. Ges., **6**, 196 (1873).
[3] Am. J. Sci. [4], **7**, 147 (1899).

these two experiments are sufficient to show that the method is accurate enough for our purpose, and the absence of boron was rendered absolutely certain by the following combustions of rosocyanine, which show that it has the same composition as curcumine. The substance burnt with great difficulty, so that in each analysis a portion of the carbon was weighed as such.

I. 0.1278 gram substance gave 0.2988 gram CO_2, 0.0058 gram C, 0.0659 gram H_2O.

II. 2.2301 gram substance gave 0.5170 gram CO_2, 0.0148 gram C, 0.1126 gram H_2O.

III. 0.1347 gram substance gave 0.3001 gram CO_2, 0.0094 gram C, 0.0660 gram H_2O.

	Calculated for $C_{14}H_{14}O_4$.	Found. I.	II.	III.
C	68.29	67.82	67.71	67.74
H	5.69	5.69	5.43	5.44

It is a noteworthy fact that the percentages of hydrogen are low in all these combustions. The same observation was made in the analyses of curcumine carried out for the first paper[1] on this subject by Menke and one of us, but a formula with less hydrogen would give results which do not agree with those found by experiment.

The molecular weight was determined in boiling acetone.

0.1041 gram substance dissolved in 35 grams acetone gave $\Delta = 0.02°$, $K = 1670$.

	Calculated for $C_{14}H_{14}O_4$.	Found.
Mol. Wt.	246.0	248.0

Properties of Rosocyanine.

Although Schlumberger states that he got fine needles, we have not succeeded in crystallizing the substance, but obtained it as a purple powder with a metallic, yellowish green reflex, which shows a close resemblance to powdered rosaniline except that the green color is yellower. A thin film of it deposited from an alcoholic solution shows a beautiful crimson rose color by transmitted light, which has no shade of magenta

[1] This Journal, 4, 77 (1882).

in it, while by reflected light it is yellowish green with a metallic lustre. It does not melt, but at about 230° changes to a greenish black substance, insoluble in alcohol, but dissolving in aqueous sodic hydrate with a bluish black color, which changes on standing to yellowish brown. This transformation of the rosocyanine begins at 200°, but goes on slowly as long as the temperature is much below 230°. On the other hand the substance should not be heated far above 230°, as in the neighborhood of 260° it decomposes into a black carbonaceous residue and a volatile red oil, which condenses in the upper part of the capillary tube, while at the same time a penetrating odor is observed. If the rosocyanine is not perfectly dry, between 230° and 260° a colorless liquid is given off, which differs from the oil both in color and smell. The study of these products will be taken up by us later. Rosocyanine is moderately soluble in ethyl alcohol, somewhat less soluble in methyl alcohol, acetone, or glacial acetic acid. All these solutions are characterized by a beautiful crimson rose color without a trace of magenta. It is not decomposed by alcohol, contrary to the statement of Schlumberger. It is almost insoluble in acetic ester, and essentially insoluble in ether, benzene, toluene, chloroform, or carbon tetrachloride. Strong sulphuric acid forms a red solution with it, from which the rosocyanine is precipitated apparently unchanged on dilution. Strong nitric acid also forms a red solution with it, but strong hydrochloric acid produces no apparent effect.

Its behavior with alkalies is very characteristic. If aqueous sodic hydrate is added to solid rosocyanine, a magnificent bluish purple solution is formed, having the color of Hofmann's violet, but if the sodic hydrate is added to an alcoholic solution, the liquid takes on a blue color like that of the solution of Prussian blue in oxalic acid. Ammonic hydrate gives a similar Prussian blue solution even in the absence of alcohol.

As it was observed that the solution of rosocyanine in an excess of aqueous potassic or sodic hydrate turned green rapidly if the amount of alkali was large, slowly if it was small, the following experiment was tried to study this de-

composition. Four grams of potassic hydrate were dissolved in a mixture of 10 cc. of alcohol with 30 cc. of water, and 0.2 gram of pure rosocyanine added. With so much alcohol present the rosocyanine dissolved very quickly, forming the characteristic fine blue solution of the salt, but in about three minutes the color had turned to green, in another three minutes it was brown, and in five minutes more it had become red. It was allowed to stand five more minutes (16 in all), and then acidified with dilute hydrochloric acid, the precipitate thus formed was washed with water, dried, and after two recrystallizations from alcohol formed yellow crystals, which, as they melted at 178° and formed a red potassium salt, must be curcumine. This experiment was repeated several times with the same result. There can be no doubt therefore that rosocyanine is converted into curcumine by standing in the cold with potassic hydrate. The hydrochloride of hydroxylamine has no action on rosocyanine.

Salts of Rosocyanine.

Ammonium Salt, $NH_4C_{14}H_{13}O_4$.—This was prepared by passing dry ammonia gas into an alcoholic solution of rosocyanine. The bluish green solution thus obtained deposited a blue precipitate, which was dried between filter papers for analysis.

0.3495 gram substance gave 15 cc. N at 20° and 760 mm.

	Calculated for $NH_4C_{14}H_{13}O_4$.	Found.
N	5.32	4.91

To judge from the blue color, this same salt was formed when a layer of rosocyanine, spread on a filter paper, was exposed to the vapor from strong ammonic hydrate by letting the two stand in a desiccator, but the action did not seem to be complete, even after it had been continued for a long time, so that this method cannot be recommended for making the salt.

Potassium Salt, $KC_{14}H_{13}O_4$.—To a saturated solution of rosocyanine in 25 cc. of absolute alcohol was added a solution of 0.2 gram of potassic hydrate in 10 cc. of alcohol. After the mixture had stood a moment, 5 or 6 drops of ether were added,

when the salt separated in purple flocks, which were filtered out, washed first with absolute alcohol and then with ether, and dried *in vacuo* for analysis. The work must be carried on rapidly to avoid the decomposition of the rosocyanine by the excess of alcoholic potassic hydrate.

I. 0.1821 gram of salt gave 0.0562 gram K_2SO_4.
II. 0.0794 gram of salt gave 0.0246 gram K_2SO_4.

	Calculated for $KC_{14}H_{13}O_4$.	Found. I.	II.
K	13.76	13.85	13.91

The potassium salt forms purple flocks, which are stable when dry, and dissolve easily in water with the characteristic blue color of the rosocyanine salts.

Barium Salt of Rosocyanine, $Ba(C_{14}H_{13}O_4)_2$.—An aqueous solution of baric hydrate was added, drop by drop, to an alcoholic solution of rosocyanine, and the beautiful blue flocculent precipitate thus obtained was filtered out, washed with alcohol, and dried *in vacuo* for analysis.

0.1204 gram of salt gave 0.0454 gram $BaSO_4$.

	Calculated for $Ba(C_{14}H_{13}O_4)_2$.	Found.
Ba	21.85	22.17

The dry salt has a purple blue color with a bronze reflex, and gives a violet mark on paper; when moistened with alcohol, it has a fine blue color. It is essentially insoluble in alcohol, and only very slightly soluble in water.

An aqueous solution of the potassium salt of rosocyanine gave characteristic precipitates with the following reagents: With calcic chloride, baric chloride, or magnesic sulphate, dark blue, the two latter precipitates being much darker than the first; with zincic sulphate, blue black; with cadmic sulphate, dark blue; with cobaltous nitrate, blue black; with nickelous nitrate, dark purple; with ferric chloride, aluminic sulphate, or chromic sulphate, dark red; with cupric sulphate or mercurous nitrate, dark red; with mercuric chloride, purple; with plumbic acetate, dark blue; with argentic nitrate, dark purple.

Acetrosocyanine, $C_{14}H_{13}(C_2H_3O)O_4$.—Two grams of rosocyanine with 30 grams of acetic anhydride were heated on the water bath to 60°, for 8 hours, in a flask with a return condenser. The liquid assumed a brownish red color as soon as the rosocyanine was added, which did not change during the eight hours' heating. At the end of that time the acetic anhydride solution was poured off from the undissolved solid and evaporated *in vacuo*, leaving a brownish red powder mixed with a little oil, which was removed by extraction with cold benzene. The powder was then dissolved in alcohol, when, as the solution evaporated, the acetrosocyanine was deposited as an amorphous brownish red powder, from which cold benzene extracted nothing. The solid which was not dissolved in the acetic anhydride also proved to be acetrosocyanine. The substance was dried *in vacuo* for analysis.

0.1241 gram substance gave 0.3031 gram CO_2 and 0.0624 gram H_2O.

	Calculated for $C_{14}H_{13}(C_2H_3O)O_4$.	Found.
C	66.67	66.59
H	5.55	5.58

Properties.—We have not succeeded in obtaining crystals of the acetrosocyanine, which appears as a brownish red powder. It has no melting point, but at 250° the color changes from reddish brown to greenish, and that a new substance has been formed is shown by the facts that it is insoluble in alcohol and unaffected by an alkali. Acetrosocyanine is very soluble in chloroform; moderately soluble in ethyl alcohol; somewhat soluble in acetone; all these solutions have a reddish brown color; essentially insoluble in ether, benzene, or ligroin. Strong sulphuric acid dissolves it partially, forming a bright red solution; strong nitric acid forms a yellow solution with it, but the action is very slow; strong hydrochloric acid does not dissolve it, but slowly imparts a darker color to the solid. An alcoholic solution of potassic hydrate decomposes it quickly, giving a greenish solution, which soon changes to yellow; a moderately strong aqueous solution of sodic hydrate produces the same effect

slowly, whereas a dilute solution acts on it only after long standing.

Action of Curcumine with Boric Acid and Alcohol.

Probable Addition Compound.—When a mixture of ten parts of curcumine with one part of boric acid was allowed to stand in the cold with alcohol for eight hours, a red solution was formed, which, after being filtered off from undissolved curcumine, was poured into ether; in this way a fine red powder was obtained which was filtered out and washed with ether. This product contains a considerable amount of boric acid, which it gives up when treated with water, being converted into the rubrocurcumine described in the next section. Three analyses were made by treating a weighed quantity with water, filtering out the organic matter, and titrating the boric acid by the mannite method,[1] but they showed that the substance had not yet been brought into a state fit for analysis, as they gave 14.7, 28, and 26 per cent of HBO_2, respectively. Further experiments will be necessary to determine whether the substances contained an impurity of boric acid, and whether the agreement of these results with those for addition products with one and with two molecules of boric acid is more than accidental. Meanwhile, it is plain that this product is not a mixture of boric acid with curcumine, rubrocurcumine, or rosocyanine, because it is converted into a waxy substance on exposure to the air—a property not shown by any of the three compounds mentioned.

Rubrocurcumine, $C_{14}H_{14}O_4$.—Two grams of curcumine, 2 grams of boric acid, and 20 grams of alcohol (95 per cent) were mixed together and allowed to stand overnight in a corked flask at ordinary temperatures. The clear red solution thus obtained was poured into 100 cc. of water, which decomposed the boric acid addition product and precipitated the rubrocurcumine in red flocks; these were quickly filtered out, washed with water until free from boric acid, and dried in a desiccator for analysis. In our earlier preparations a more elaborate method was used, consisting in evaporating

[1] L. C. Jones: Am. J. Sci. [4], 7, 147 (1899).

the red alcoholic solution in a desiccator at ordinary temperatures until the rubrocurcumine began to form a crust on the edge of the dish, when the solution was poured into 20 cc. of ether and the precipitated rubrocurcumine washed with water as before. The object of this treatment was to remove any unaltered curcumine, but was proved to be unnecessary, because the amount of boric acid used was enough to convert all the curcumine into rubrocurcumine.

0.0737 gram substance gave 0.1662 gram CO_2, 0.0049 gram C, and 0.0392 gram H_2O.

	Calculated for $C_{21}H_{18}O_4$.	Found.
C	68.29	68.15
H	5.69	5.90

Properties of Rubrocurcumine.—It was not obtained in crystals, but forms a vermilion powder of a less dark red color than the addition product. It appears to be unstable, as a sample, on standing at ordinary temperatures for two weeks, passed back into curcumine to judge from its behavior with dilute sulphuric acid or alkalies. The same change to curcumine takes place in a few minutes when rubrocurcumine is boiled with water. It does not melt, but, when heated to 200°, gradually takes on the purple color with a metallic green reflex of rosocyanine; at 240° the change takes place more rapidly and completely. That the product was rosocyanine was shown by the crimson rose color of its alcoholic solution and the intense blue color which appeared when it was treated with an alkali. If the temperature is carried to 250° or higher, a product insoluble in alcohol is formed, which dissolves in alkalies with a greenish color, and is probably identical with the substance obtained by heating rosocyanine. Heating rubrocurcumine with dilute sulphuric acid converts it easily into rosocyanine; but it is hardly necessary to state that these reactions can be obtained only with fresh, unaltered preparations. It is very soluble in alcohol, giving a red solution distinct in color from the crimson rose solution of rosocyanine; soluble in methyl alcohol, ether, or acetone; somewhat soluble in chloroform; almost insoluble in

benzene or toluene. Strong sulphuric acid dissolves it with a bright red color; strong nitric acid forms with it a yellow solution; strong hydrochloric acid dissolves it only slightly, giving a violet solution changing very quickly to red. An aqueous solution of an alkali dissolves the rubrocurcumine with a royal purple color, that is, the solution is of a redder purple than that of the salt of rosocyanine. This solution quickly changes its color to brown, the rubrocurcumine apparently being converted into curcumine.

Acetrubrocurcumine, $C_{14}H_{13}(C_2H_3O)O_4$.—One gram of rubrocurcumine was allowed to stand at ordinary temperatures with 10 grams of acetic anhydride for 8 hours. The rubrocurcumine went into solution in less than half an hour, forming a yellowish red liquid. The acetic anhydride was evaporated off in a desiccator over sodic hydrate, and the yellow powder left recrystallized from alcohol till it showed the constant melting point, 245°, when it was dried *in vacuo* for analysis.

0.1479 gram substance gave 0.3315 gram CO_2, 0.0084 gram C, and 0.0756 gram H_2O.

	Calculated for $C_{14}H_{13}(C_2H_3O)O_4$.	Found.
C	66.67	66.81
H	5.55	5.68

Properties of Acetrubrocurcumine.—It forms orange yellow prismatic needles, which melt at 245°. The fact that this acet compound melts, whereas rubrocurcumine itself is infusible, may be explained on the supposition that in the latter body the hydroxyl is converted into the oxide oxygen of the infusible rosocyanine at a temperature below where its melting point would lie, whereas the acetoxyl of the former compound prevents its transformation into rosocyanine. Very soluble in acetone, or chloroform; somewhat soluble in methyl alcohol, ether, or glacial acetic acid; not very soluble in cold alcohol, more so in hot; slightly soluble in benzene; insoluble in ligroin. Strong sulphuric acid dissolves it with a bright red color; strong nitric acid gives a yellow solution with it; strong hydrochloric acid has no apparent effect. An

aqueous solution of sodic hydrate has no effect on it in the cold, but, if heated with it, saponifies it, and then apparently converts it it into curcumine.

Experiments on the Preparation of Rubrocurcumine.

Under this head we have studied only the effect of water.

(1) One-tenth of a gram of curcumine was dissolved in absolute alcohol and 0.2 gram of boric acid added. The red color of rubrocurcumine appeared very soon, even in the cold, and a considerable amount of it was obtained after the mixture had stood for several hours in the cold or been heated for a few minutes.

(2) One-tenth of a gram of curcumine and 0.2 gram of boric acid were mixed with 10 cc. of a mixture of equal parts of alcohol and water. No rubrocurcumine was formed in the cold, even after standing for several weeks, but upon heating some of the mixture in a sealed tube to 160° for five hours fully 25 per cent of the curcumine was found to be converted into rubrocurcumine.

(3) The same weights of curcumine and boric acid were mixed with 10 cc. of water, but even after heating the mixture in a sealed tube to 160° for five hours only a very small amount of rubrocurcumine was formed.

These three experiments show that the presence of water interferes seriously with the formation of rubrocurcumine, but that it is possible to obtain it even without the help of alcohol.

Experiments on the Preparation of Rosocyanine.

The influence of water in preventing the formation of rosocyanine was shown in our preparations of it from curcumine, boric acid, sulphuric acid, and alcohol, where a yield of 95 per cent was obtained with absolute alcohol, 80 per cent with common (95 per cent) alcohol, and only 60 per cent with a mixture of equal parts of alcohol and water.

The alcohol used in the preparation of rosocyanine seems to take no part in the reaction, but to act only as a solvent, because a mixture of curcumine, boric acid, dilute sulphuric

acid, and pure acetone gave rosocyanine, and it was also obtained from curcumine, boric acid, and glacial acetic acid, when the last substance not only acted as a solvent but also replaced the dilute sulphuric acid.

This experiment with acetic acid was tried before the discovery of rubrocurcumine had shown us that boric acid acts on curcumine in presence of alcohol alone, and formed part of a series on the influence upon the reaction of those substances which increase the acid nature of boric acid, and which we thought then might be necessary to cause the boric acid to unite with the curcumine. In addition to acetic acid, glycerine and mannite[1] act in this way, the last imparting to boric acid a taste as sour as that of citric acid and the power of decomposing carbonates. One gram of curcumine, one of boric acid, 0.5 gram of mannite, and 10 cc. of 50 per cent alcohol were warmed together for 5 minutes, when the solution had turned red, although not quite the pure crimson rose of rosocyanine, but on the addition of an alkali the intense blue, characteristic of the rosocyanine salts in alcoholic solution, was developed. For greater certainty it was compared with the color obtained by adding alkali to a solution of rosocyanine in 50 per cent alcohol, and found identical with it. Experiments such as this gave rosocyanine in three cases, but in a fourth only rubrocurcumine. Ten cc. of a 30 per cent solution of glycerine in water were mixed with 0.1 gram of curcumine, 0.2 gram of boric acid, and a few drops of alcohol. After standing in the cold for a few minutes the crimson color of rosocyanine appeared, and its presence was confirmed by the blue color produced with an alkali. The same result was obtained in a parallel experiment, in which the alcohol was omitted. These experiments show that mannite or glycerine can take the place of sulphuric or hydrochloric acid in the formation of rosocyanine. It seems probable, however, that the place of the strong mineral acid is taken by the boric acid, intensified by the mannite or glycerine, rather than by the polyatomic alcohols themselves.

[1] L. C. Jones: Am. J. Sci. [4], **7**, 147; D. Klein: Bull. Soc. Chim. [2], **29**, 198 (1878); Lambert: Compt. rend., **108**, 1016 (1889).

Monomethylcurcumine, $C_6H_3(OCH_3)_2C_7H_7O_2$.—This substance was made from the monopotassium salt of curcumine discovered by Menke and one of us,[1] which we prepared as follows: Five grams of potassic carbonate and 5 grams of curcumine were boiled with 100 cc. of 99 per cent alcohol for half an hour, after which the deep red solution was filtered and 300 cc. of ether added to it, a few cc. at a time, with constant shaking. The monopotassium salt, which separated in fine red needles, was filtered out, washed with ether, and dried.

Three grams of this monopotassium salt were dissolved in 10 cc. of absolute methyl alcohol, 10 grams of methyl iodide added, and the mixture shaken on a shaking machine for 2 days. It was then allowed to stand in the cold for 2 days to give time for the crystallization of the potassic iodide, and, after this had been filtered out, the solution was evaporated *in vacuo*. The residue was a red tar, which, after standing for 2 days, hardened to a stiff mass; this was scraped out of the dish with a platinum spatula, thoroughly pulverized in a mortar, and washed with water until it gave no test for an iodide. Upon drying, it appeared as a brownish red powder which showed no sharp melting point. Accordingly, to purify it further, one gram was treated with 10 cc. of pure ether, the yellow solution thus formed evaporated *in vacuo*, and the extract, an orange colored oil, dissolved in 2 cc. of ordinary alcohol. The solution was filtered to remove some white needles, which appeared in such minute amount that we could not determine their nature, and then to the filtrate was added, drop by drop, with constant stirring, 20 cc. of a 20 per cent solution of sodic chloride in water. Under these conditions the monomethyl ether of curcumine crystallized out in very small, orange yellow needles, melting sharply at 145°, which were washed and dried *in vacuo*.

0.1355 gram substance gave 0.3441 gram CO_2 and 0.0751 gram H_2O.

	Calculated for $C_{14}H_{12}CH_3O_4$.	Found.
C	69.23	69.25
H	6.15	6.16

[1] THIS JOURNAL, 4, 77 (1882).

Properties of Monomethylcurcumine.—It crystallizes in small, orange yellow needles, which melt at 145°. It is soluble in ethyl or methyl alcohol, chloroform, acetone, benzene, acetic ester, or glacial acetic acid; somewhat soluble in ether; essentially insoluble in ligroin or carbon tetrachloride. It dissolves in aqueous sodic hydrate, owing to the formation of a soluble salt, but it is not acted on by sodic carbonate.

Oxidation of the Monomethylcurcumine.—As in this substance the methyl group had replaced the more acid atom of hydrogen, it was of interest to determine whether this was contained in a hydroxyl attached to the benzene ring or to the side chain. For this purpose the substance was oxidized as follows: One gram of the monomethyl ether of curcumine was dissolved in aqueous potassic hydrate, and a 5 per cent solution of potassic permanganate added in small quantities at a time. Decolorization took place at first quickly, later more slowly, and after a very slight excess had been added, the mixture was allowed to stand overnight. The permanganate was then destroyed by the addition of one or two drops of alcohol, the hydrate of manganese filtered out, thoroughly washed, and the filtrate, after acidification with dilute hydrochloric acid, extracted with ether. The ether extract, when evaporated to dryness, yielded a white powder which, after two recrystallizations from alcohol, showed the constant melting point, 178°. It is, therefore, veratric acid, the melting point of which is given by Graebe[1] and Borgmann and Koerner[2] as 179°.5, while Goldschmiedt[3] states that it softens at 179° and melts at 181°. Our somewhat lower result may easily be due to a difference in the thermometers. As veratric acid is $C_6H_3(OCH_3)_2COOH$, it follows that the more acid hydroxyl in curcumine is the one in the vanillin part of the molecule, that is, the one attached to the benzene ring.

Formation of Monomethylrosocyanine, $C_{14}H_{13}CH_3O_4$.—One gram of the monomethyl ether of curcumine was dissolved in a mixture of 10 grams of absolute alcohol, 0.5 gram of strong

[1] Ann. Chem. (Liebig), **168**, 282 (1871).
[2] Gazz. chim. ital., **1876**, 142.
Monats. Chem., **6**, 378 (1887).

sulphuric acid, and 0.5 gram of boric acid. A crimson color appeared a few seconds after the materials were mixed, but to complete the reaction the solution was heated for half an hour on the steam bath. The intense crimson solution obtained in this way was poured into a large excess of water, which precipitated a powder looking like rosocyanine. This was washed, dried, and extracted with ether as long as a colored extract was formed, to remove unchanged monomethylcurcumine, after which it was dried for analysis.

0.0837 gram substance gave 0.2124 gram CO_2 and 0.0510 gram H_2O.

	Calculated for $C_{18}H_{18}O_4$.	Found.
C	69.23	69.21
H	6.15	6.77

Properties of Monomethylrosocyanine.—It forms a purple powder with a metallic yellowish green reflex, looking much like rosocyanine, and is soluble in alcohol, acetone, or glacial acetic acid with a crimson color, not so brilliant as that obtained with rosocyanine; nearly insoluble in ether; and insoluble in benzene, ligroin, or water. Strong sulphuric acid dissolves it with a beautiful red color, changing slowly to brown; strong nitric acid gives a brownish yellow color, changing slowly to yellow; strong hydrochloric acid dissolves it slightly with a red color. Alkalies at first have no effect either in dissolving it or changing its color, but on long standing, caustic alkalies give a red solution, apparently of a salt of monomethylcurcumine. This behavior is what would be expected, as from our study of rosocyanine it is evident that its monomethyl ether can contain no free hydroxyl.

Application of the Rosocyanine Reaction to some other Derivatives of Curcumine.

Protocurcumine is the name we propose for the substance formed by removing one methyl group from curcumine. Its formula is $C_6H_3(OH)_2C_7H_7O_2$, and it stands in the same relation to curcumine that protocatechuic acid does to vanillic acid. This substance, which will be described in detail in a

later paper, gave with boric acid, sulphuric acid, and alcohol, a crimson solution, turned blue by an alkali. On the other hand, the dimethyl ether, or the dihydride of curcumine, gave no visible reaction when warmed with boric acid, sulphuric acid, and alcohol. The significance of the experiments with these substances has been discussed in the introduction to this paper.

The investigation of rosocyanine will be continued by us in several directions, but must be preceded by the determination of the constitution of curcumine, toward which we have made good progress.

CAMBRIDGE,
January 2, 1908.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

STUDIES IN CATALYSIS.
VI.[1] THE CATALYSIS OF IMIDOESTERS.[2]

BY HERMANN I. SCHLESINGER.

PART I.

The Velocity of Saponification of the Alkyl Imidobenzoates in the Presence of Acids, and Their Degree of Ionization.

In the well-known catalysis of ordinary acid esters by means of acids, according to the equation

$$RCOOR' + HOH = RCOOH + HOR' \qquad (1),$$

the "catalytic" functions of the acid are considered by Stieglitz[3] to consist simply in the formation of a salt of the ester and, thereby, in the increase of the concentration of the positive ion, which is considered to constitute the "active mass" of the ester. This increase, on account of the small original ionization of the ester, is directly proportional to the salt formed and, hence, to the acid used in the reaction. For the experimental investigation of the correctness of this theory,

[1] Articles I.-V., THIS JOURNAL, **39**, 29, 166, 402, 437, 586.

[2] This article was accepted as a dissertation in July, 1905, and sent to the editor in September, 1907.

[3] Report of the Congress of Arts and Science, **4**, 278 (1904); THIS JOURNAL, **39**, 29 (1908).

the closely related group of imidoesters, RC(NH)OR′, was employed, since for these substances the requisite experimental and mathematical data could be obtained. These esters form well defined salts with acids; the rate of their decomposition with water, according to the equation

$$RC(:NH)OR' + HOH = RCOOR' + NH_3 \qquad (2),$$

is accelerated considerably by the addition of an acid. The investigations carried out in this laboratory by Derby and McCracken[1] showed that, as a matter of fact, the velocity of decomposition of the imidoesters in this direction is directly proportional to the concentration of the imidoester salt present at any moment. As the experiments were carried out in dilute solutions (one-tenth to one-fortieth molar) in which the salts are almost completely ionized, the conclusion was drawn that the "active mass" of the imidoester would almost surely prove to be, not the total salt concentration, but only the ionized portion of the salt. With the purpose of testing rigorously this important point in the conclusion, the following investigation of the relation between the velocity of saponification of the hydrochlorides of the alkyl imidobenzoates and their respective degree of ionization was undertaken by me at the suggestion of Professor Stieglitz and carried out under his direction. The results obtained, in solutions varying from half molar to twentieth molar, not only showed the correctness of the conclusion that the substance reacting with water according to (2) to give an acid ester and ammonia actually is the positive ion of the salt, but, further, brought to notice another most striking parallelism in the behavior of the imidoesters and ordinary esters towards water. As is well known, the catalysis of the esters, as well as of cane sugar and similar substances, is increased by the presence of neutral salts, which produce the so-called "salt effect" studied by Spohr,[2] Arrhenius,[3] Euler,[4] and others. This "salt effect" was found by these

[1] *Loc. cit.*
[2] J. prakt. Chem. [2], **33**, 270.
[3] Z. physik. Chem., **4**, 226 (1889).
[4] *Ibid.*, **33**, 348 (1900).

investigators to be proportionate to the concentration of the salt added, except in the case of very dilute solutions. The results obtained by me indicate that the "catalysis" of imidoester salts is subject to exactly the same kind of "salt effect," except that, in this case, the salts involved in the reaction, *viz.*, the salt of the imidoesters and the ammonium chloride formed in the decomposition, themselves produce the acceleration—an "auto effect," as it might be called.

The "salt effect" is produced most markedly on substances which are but little ionized,[1] and the change in the speed of a catalysis in which water is primarily involved is ascribed particularly to the increase in the "active mass" or the dissociation of water itself in the presence of salts.[2] This explanation would account perfectly also for the "salt effect" in the decomposition of the imidoester salts—since the active mass of the water is one of the factors in the velocity formula (see equation 2).

In view of the facts established, then, since the decomposition of an imidoester into an ordinary ester is proportional to the concentration of the positive ion, the correct equation for this reaction becomes

$$C_6H_5C(:\overset{+}{N}H_2)OCH_3 + HOH = C_6H_5COOCH_3 + \overset{+}{N}H_4 \quad (2').$$

That the analogy between the ordinary esters and the imidoesters is practically complete will be shown in Part II. by proving that the imidoesters are decomposed also by means of alkalis into nitriles and alcohols, with a velocity directly proportional to the concentration of hydroxyl ion—exactly as is the case in the saponification of esters.[3]

[1] Arrhenius: *Loc. cit.*

[2] Euler: *Loc. cit.*

[3] By the action of absolute alcohols on imidoester salts Reitter and Hess (Ber. d. chem. Ges., **40**, 3020) obtained ortho acid esters:

$$CH_3C(:NH_2Cl)OC_2H_5 + 2HOC_2H_5 \longrightarrow CH_3C(OC_2H_5)_3 + NH_4Cl.$$

The difference in the result of this action and that of water on such salts suggested that the formation of ortho esters would be found due to the following sequence of reactions:

$$CH_3C(:\overset{+}{N}H_2)OC_2H_5 + HOC_2H_5 \longrightarrow CH_3C(\overset{+}{N}H_2)(OC_2H_5)_2 \longrightarrow CH_2:C(OC_2H_5)_2 + \overset{+}{N}H_4;$$

and

$$CH_2:C(OC_2H_5)_2 + HOC_2H_5 \longrightarrow CH_3C(OC_2H_5)_3.$$

As a matter of fact Reitter has isolated, in the case of cyanacetic ester, a compound $C(OC_2H_5)_2:CH.CO_2C_2H_5$ (*loc. cit.*, **40**, 3358), either as an intermediate or a final

EXPERIMENTAL.

1. The Hydrochloride of Ethyl Imidobenzoate.

The velocity of the decomposition by water of the hydrochloride of ethyl imidobenzoate, according to the equation

$$C_6H_5C(:\overset{+}{N}H_2)OC_2H_5 + H_2O = C_6H_5COOC_2H_5 + \overset{+}{N}H_4 \quad (3),$$

was determined at 25°, in solutions containing one mole in 2, 4, 5, 10, and 20 liters, respectively. The solutions were placed in a bath of 320 liters capacity, whose temperature was kept at 25° (±0.01) by means of an Ostwald thermostat. The method of analysis used was the one described by Derby:[1] by means of a pipette, a measured portion (25, 10, or 5 cc.) of the salt solution was rapidly run into a known amount of standard sodium hydroxide solution (an excess of this was used); the free imidoester liberated was removed by three extractions with carbon tetrachloride (15, 10, and 5 cc., respectively); and the excess of sodium hydroxide in the aqueous residue determined by titration with standard hydrochloric acid. Methyl orange was used as indicator.

A mixture of a benzimidoester hydrochloride and ammonium chloride behaves under this treatment exactly as does a mixture of free hydrochloric acid and ammonium chloride; the imidoester salt neutralizes part of the added alkali, while

product. On the basis of this hypothesis of an *intermediate* product, the reaction would not work with the imidoester salts of a tertiary acid, like benzimidoesters, and a reply of Professor Reitter to a private inquiry has confirmed the correctness of this surmise, as far as preliminary experiments go. Professor Reitter, with Dr. Hess, has kindly consented to our taking up this part of the problem as well as the physicochemical study of the formation of ortho esters, while he and his collaborators will develop it from the preparative side and endeavor to isolate the compounds $C_6H_5CH:C(OR)_2$ in the action of alcohols on the imidoester salts of benzyl cyanide. These facts are mentioned here because the work on saponification and esterification, etc., is being taken up by us along these lines with aliphatic esters and imidoesters of primary, secondary, and tertiary acids, *as such reactions may form parallel or even the main intermediate actions* in some cases of ordinary saponification, etc. It may be recalled that McCracken and I have already found that the velocity of decomposition of imidoester salts of phenylacetic acid is exceedingly high, very much higher than that of aromatic salts, and it should be said that Dr. Blunt has obtained a similar result for the action of ammonia on such salts. These and a large number of other facts recorded by different investigators, (Cf. Nef, Standinger, Wilsmore) which will be discussed at the proper time, promise to lead to a deeper insight into all the various sides of these problems than has hitherto been obtained.—JULIUS STIEGLITZ (May, 1908).

[1] THIS JOURNAL, **39**, 437 (1908)

this is not true in the case of ammonium chloride; unlike the free imidoester, ammonia in very dilute solution is not appreciably removed by carbon tetrachloride, and hence, since methyl orange is sensitive to it as well as to the fixed alkali, it does not affect the titration. Thus, if b cc. of N/10 sodium hydroxide are added to v cc. of the salt solution and d cc. of N/10 hydrochloric acid are required after the extractions to neutralize the excess of alkali, the concentration of the unchanged salt is proportional to $(b—d):v$. The observed values given below were obtained in this way.

The velocity constants were calculated according to the equation for a monomolecular reaction,

$$\frac{dx}{dt} = K_v(C - x) \qquad (4),$$

and

$$K = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (5).$$

As Derby[1] has shown, the substance undergoing change is the salt or its positive ion alone, and not the free base liberated by the hydrolytic action of the water present. Inasmuch as the degree of hydrolysis is less than one per cent for ordinary dilutions, the free base liberated is a negligible quantity and the salt may be put equal to the total quantity of unchanged substance.

For each concentration for which the velocity was determined, the degree of ionization of the salt was found experimentally. This value, in a given experiment with given concentration of salt, may be considered a constant for the experiment; although the imidoester salt used is growing smaller in concentration during the course of the reaction, each molecule is being replaced by one of ammonium chloride, and the total electrolytic content in this way remains unchanged. Under these conditions, according to the laws of isohydric solutions, the degree of ionization of the imidoester salt may be considered practically a constant for the whole period of a velocity determination. The value of the ionization factor

[1] *Loc. cit.*

will be incorporated in the final velocity constant in the manner discussed below (p. 729); for each determination the velocity constant, independent of the ionization, will, however, first be calculated simply according to equation (5).

In the following tables, v gives the volume in liters containing one gram molecule of the imidoester salt, w gives the portion in cc. used for each titration at the time indicated under t. This line contains the time in minutes, from the time of the first titration to the moment when the first quantity (w) of solution was introduced into the excess of alkali; in line 2, under $(C-x)$, will be found the cc. of N/10 alkali neutralized by the unchanged imidoester salt contained in the w cc. used for the titration. The concentration of the unchanged substance, $(C-x_1)$, etc., is proportional to this value. In line 3, the velocity constants calculated according to equation (5) are given, the values being 43430 times the true constant. All the determinations were made, as mentioned, at 15° (±0.01).

As was anticipated, the tables show that the velocity of decomposition is very markedly dependent on the concentration of the salt used. To determine rigorously whether this result is due to the fact that only the positive ion of the salt is reacting and not the nonionized molecule, the degree of dissociation of the hydrochloride of ethyl imidobenzoate in the various concentrations used was determined by the conductivity method. Owing to the fact that the salt is very rapidly decomposed by water at 25°, the conductivity measurements were made at 0°; at this temperature, much less difficulty was experienced in obtaining satisfactory results, since the rate of decomposition is slow. The work of H. C. Jones[1] on the degree of ionization of chlorides shows that this value is practically the same at 0° as at 25°; hence the values obtained at 0° for the hydrochloride used may be employed to calculate the relations desired at 25°. On account of the hydrolytic dissociation of the hydrochloride according to the equation

$$C_6H_5C(NH_2Cl)OC_2H_5 \rightleftarrows C_6H_5C(NH)OC_2H_5 + HCl \qquad (6),$$

[1] This Journal, **28**, 1442 (1901).

The Hydrochloride of Ethyl Imidobenzoate.

Table Ia.

v = 20. w = 25 cc. Mean, 43430 K_v = 136.

t	0	60	90	120	150	180	210
$(C-x)$	11.77	9.75	8.93	8.10	7.35	6.73	6.04
43430 K_v	....	136	133	135	136	135	138

Table Ib.

v = 20. w = 25 cc. Mean, 43430 K_v = 135.

t	0	30	60	90	180	210	240
$(C-x)$	12.01	10.97	9.98	9.09	6.79	6.11	5.18
43430 K	....	131	134	134	137	140	135

Table IIa.

v = 10. w = 10 cc. Mean, 43430 K_v = 132.

t	0	30	60	90	120	150	286	315	375
$(C-x)$	9.60	8.74	8.03	7.35	6.64	6.04	4.13	3.69	3.10
43430 K_v	....	136	129	129	134	135	128	132	132

Table IIb.

v = 10. w = 10 cc. Mean, 43430 K_v = 133.

t	0	30	60	90	120	150	240	270	300
$(C-x)$	9.75	8.89	7.98	7.35	6.67	6.20	4.70	4.32	3.87
43430 K_v	....	134	(145)	136	136	131	132	131	134

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The Hydrochloride of Ethyl Imidobenzoate.

Table IIIa.

$v = 5$. $w = 10$ cc. Mean, 43430 $K_v = 122$.

t	0	30	60	90	120	240	285	330
$(C-x)$	19.24	17.57	16.24	15.04	13.61	9.84	8.57	7.55
43430 K_v	....	(131)[1]	123	119	125	121	123	123

Table IIIb.[2]

$v = 5$. $w = 5$ cc. Mean, 43430 $K_v = 126$.

t	0	30	60	90	120	153	180	210
$(C-x)$	9.61	8.74	8.05	7.41	6.79	6.14	5.79	5.17
43430 K_v	....	(137)	128	125	126	127	122	128

Table IIIc.

$v = 5$. $w = 10$ cc. Mean, 43430 $K_v = 121$.

t	0	25	55	85	115	145	236	265
$(C-x)$	19.15	17.79	16.48	15.09	13.95	12.77	9.82	9.27
43430 K_v	....	(128)	119	122	120	121	123	119

Table IVa.

$v = 4$. $w = 10$ cc. Mean, 43430 $K_v = 120$.

t	0	45	75	105	210	240	270	300	345
$(C-x)$	24.27	21.22	19.71	18.17	13.59	12.64	11.47	10.71	9.59
43430 K_v	....	(130)	120	120	119	120	121	119	123

[1] The first titrations at the end of 25 to 30 minutes often gave an abnormal constant, high or low, probably due chiefly to the fact that a small difference in the titration, $(C-x)$, produces a large difference in the value K_v.

[2] The temperature of the bath during this determination was about 0.03° too high. This probably accounts for the high value of K_v.

The Hydrochloride of Ethyl Imidobenzoate.

Table IVb.

$v = 4$. $w = 10$ cc. Mean, 43430 $K_v = 119$.

t	0	30	60	90	121	255	285	316	345
$(C-x)$	24.17	22.44	20.50	18.94	17.36	12.12	11.19	10.06	9.43
43430 K_v	....	(107)	119	118	119	118	117	120	119

Table Va.

$v = 2$. $w = 5$ cc. Mean, 43430 $K_v = 107$.

t	0	30.2	60	90	241	270	300	330
$(C-x)$	22.89	21.24	19.89	18.26	12.86	11.86	10.90	10.00
43430 K_v		108	103	109	104	106	107	109

Table Vb.

$v = 2$. $w = 5$ cc. Mean, 43430 $K_v = 105$.

t	0	29	59	89	119	244	269	299	332
$(C-x)$	24.33	22.74	21.21	19.78	18.15	13.67	13.03	11.95	11.09
43430 K_v	....	101	101	103	107	104	105	107	106

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it was necessary to determine the conductivity by Bredig's method[1] in the presence of an excess of the free base sufficiently great to neutralize the acid liberated and small enough to have no appreciable conductivity of its own in the presence of its salt. Because of the instability of the salt in aqueous solution, the following methods of operation were used: In the case of the more concentrated solutions (N/10–N/2) a small cell of the Kohlrausch type was employed. The cell had a capacity of about 4 cc.; the electrodes, whose diameter was about 7 mm., were, when fully immersed, separated by a column of liquid about 35 mm. in length and 5 mm. in diameter. Solutions of the free base of the approximate concentrations, N/40 and N/80, were made up and kept at —5°. The salt was weighed out into a dry graduated 5 cc. flask, the flask filled with one or the other of the free base solutions, and the whole well mixed and cooled to zero; the mixture was then poured rapidly into the small cell, which was kept in a zero bath, and the resistance of the solution measured by means of a Kohlrausch bridge and telephone. In the case of the more dilute solutions (N/20–N/256), an ordinary Arrhenius cell was used. The solutions of free base were kept in 50 cc. flasks calibrated for delivery; the salt was weighed out in a small beaker, the solution of free base poured over it from the graduated flask, and the whole well mixed and cooled to about —0°.5. This solution was then poured into the Arrhenius cell and its resistance measured in the usual way. In all the experiments, a calibrated thermometer was used, and the resistance measured at exactly 0°. It was found that the resistance remained constant for longer than 10 minutes, thus showing that no appreciable decomposition had set in.

In Table VI., the results obtained for the conductivities are given. Column 1 contains the volume in which one gram molecule of salt is dissolved; in columns 2 and 5 the molecular conductivities (Λ_v) in the presence of an excess of one-eightieth and one-fortieth normal free base, respectively, will be found; in column 3 are given the differences (Δ) which must be added to the molecular conductivities (Λ_v) to obtain

[1] Z. physik. Chem., **13**, 213 (1894).

the conductivity (Λ_∞) for the salt at infinite dilution. According to Ostwald[1] and Bredig,[2] these differences are considered to have a fairly constant value for the various classes of salts in solutions varying in concentration from N/1024 to lower concentrations. The differences (Δ) used in the following table were calculated from Bredig's values[3] by multiplication, first by the factor 1.065 to reduce reciprocal mercury units to reciprocal ohms, and second, by the factor 0.45, which is the approximate correction (within two or three per cent) for the change of temperature from 25° to 0°.[4] Briefly,

$$\Delta_0 = \Delta_{25^\circ} \times 1.065 \times 0.45.$$

In columns 4 and 6 we have placed the molecular conductivities at infinite dilution (Λ_∞) as calculated from Δ_v and Λ_v. In column 7, the degree of ionization (α_v) of the salt is given for each concentration.

Ethyl Imidobenzoate Hydrochloride.

Table VI.

1	2	3	4	5	6	7
V.	Λ_v.[5]	Δ.	Λ_∞.[8]	Λ_v.[6]	Λ_∞.	$\alpha_v \times 100$.
2	30.6	....	....	30.5	....	56.6
4	37.0	....	....	37.0	....	68.5
5	38.7	....	....	38.7	....	71.7
10	43.6	....	....	43.6	....	80.7
20	....	7.7[7]	....	45.7	53.4	84.6
32	47.0	6.7	53.7	47.3	54.0	87.3
64	48.7	5.3	54.0	49.1	54.4	91.0
128	50.4	3.8	54.2	50.4	54.2	93.3
		Mean,	54.0	Mean,	54.0	

If the observed velocity constants, K_v (column 3, Table IV.) for the decomposition of the hydrochloride of ethyl imidobenzoate in varying concentrations be divided by the

[1] Z. physik. Chem., **2**, 840.

[2] *Ibid.*, **13**, 198 (1894).

[3] *Loc. cit.*

[4] Stieglitz and Upson: THIS JOURNAL, **31**, 469 (1904).

[5] These are the values for Λ_V when an excess of N/80 base was used.

[6] These are the values for Λ_V when an excess of N/40 base was used.

[7] Found by extrapolation.

[8] This column contains the values of Λ_∞ calculated from Λ_V in column 2; those calculated from Λ_V in column 5 will be found in column 6.

corresponding degree of ionization,[1] we obtain as the *apparent* velocity of decomposition of the positive ion,

$$K_{ion\ app.} = \frac{K_v}{\alpha_v} \qquad (7).$$

This gives a series of values representing the velocity constants (column 4, Table VII.), calculated on the assumption that only the positive ion of the salt is undergoing decomposition by water. As is well known, however, the speed of reactions in which water is an active agent is greatly accelerated by the presence of neutral salts.[2] This effect may be due to an increase, by the salt, in the active mass of the water;[3] but, whatever the cause, the fact remains that neutral salts have this influence and that, except for extreme dilutions, the effect is fairly proportional to the concentrations of the salt used. As a general rule, it is true also that there is comparatively little difference in the effect of analogous inorganic salts.[4] In order, in our case, to determine this "salt effect" and find the true velocity of decomposition of the positive ion, K_{ion}, when, hypothetically, there is no salt present and hence no "salt effect," we may consider the apparent velocities, $K_{ion\ app.}$ (given in Table VII., column 4), for 0.05, 0.1, and 0.20 molar solutions, respectively. Inspection shows at once that the "salt effect" for every 0.05 mole salt may be taken to be 3 in the terms of the same units

[1] In the decomposition of the imidoester salt, ammonium chloride replaces the hydrochloride of the imidoester. According to the laws of isohydric solutions, however, the degree of ionization of the unchanged imidoester salt will remain practically unaltered, since the total electrolyte content remains constant. The somewhat greater degree of ionization of ammonium chloride will have a negligible effect.

[2] Part I., page 720.

[3] Euler: Z. physik. Chem., **32**, 348 (1900).

[4] Arrhenius: *Loc. cit.* This may explain why the change of the imidoester salt into ammonium chloride does not seem to change the "salt effect" to any great extent. In Tables I.–V. K_v does not change much in the six hours during which velocities were measured. It is peculiar, however, that the "auto effect" of the hydrochloride of methyl imidobenzoate seems to be twice as great as for the hydrochloride of ethyl imidobenzoate. A thorough investigation of the effect of different salts is being carried out by Miss Edith E. Barnard.

NOTE.—Miss Barnard's work has now been completed. A more reliable method of determining Λ_∞, and consequently the degrees of ionization, employed by us has given very accurate results, confirming the fact that the salt effect is proportionate to the ion concentrations, and that the velocity of decomposition is otherwise proportionate to the ionized part of imidoester salts.—J. STIEGLITZ.

as are used for K. Then for the hypothetical case, where the salt concentration is 0, we would have, since here there is no "salt effect,"

$$K_{ion} = 161-3;$$
$$K_{ion} = 158 \qquad (8).$$

From this we see that the "salt effect" consists in an acceleration of the velocity of 3/158, or practically 2 per cent for every 0.05 gram molecule of salt present. Considering the effect as proportional to the total salt present, we may write

$$K_{ion\ app.} = K_{ion} \times (1 + \frac{m}{0.05} \times 0.02) =$$
$$158 \times (1 + \frac{m}{0.05} \times 0.02) \qquad (9).$$

Combining equations (7), (8), and (9), we find that we can calculate the velocity with which the hydrochloride of ethyl imidobenzoate should be decomposed by water at any concentration. The following equation expresses the relationship:

$$K_{calc.} = K_{ion} \times \alpha_v \times \left(1 + \frac{m \times 0.02}{0.05}\right) \qquad (10),$$

$$= 158 \times \alpha_v \times \left(1 + \frac{m \times 0.02}{0.05}\right) \qquad (10').$$

In this equation, m is the concentration of the imidoester salt in gram molecules per liter and α_v is the degree of ionization. The values for $K_{calc.}$ are found in column 5, Table VII.

It is very likely, however, that the true "salt effect" is essentially due to the ionized part of the salt present and not to the total salt;[1] under these circumstances, the following equation should more correctly represent the facts:

$$K_{calc.} = K_{ion} \times \alpha_v \times \left(1 + \frac{m \times 0.02 \times \alpha_v}{0.05 \times \alpha_{0.05}}\right) \qquad (11),$$

$$= 158 \times \alpha_v \times \left(1 + \frac{m \times 0.02 \times \alpha_v}{0.05 \times 0.846}\right) \qquad (11').$$

[1] Arrhenius: *Loc. cit.* Euler: *Loc. cit.*

The values calculated in this way are found in the last column of Table VII. It is obvious that a striking agreement exists between the theoretical velocities calculated according to either equation (10′) ($K_{calc.}$ in column 5) or equation (11′) ($K'_{calc.}$ in column 6) and the velocities actually observed (K_v in column 3). The greatest deviation, in fact, from the theoretical values is 3.5 per cent., which is well within the limits of experimental errors.

Table VII.

1	2	3	4	5	6
m.	100 α_v.	43430 K_v.	$43430 \times \frac{K_v}{\alpha_v}$.	$43430 \times K'_{calc.}$	$43430 \times K_{calc.}$
0.50	56.6	105	185.5	107	101.5
0.25	68.5	120	175	119	117
0.20	71.7	121.5	169.5	122.5	121
0.10	80.7	132.5	164	132.5	132
0.05	84.6	136	161	136	136
0.00	....	....	158[1]	....	....

The "salt effect" may be represented graphically in the following diagram, in which the velocity constant $K_v : \alpha_v$, with no correction for the "salt effect" (column 4), is given on the horizontal coördinate, and the total concentration of ionized salt is given on the ordinate ($C_{ions} = m \times \alpha$). The curve represents an almost straight line, showing an acceleration directly proportional to the concentration of the ionized salt present.

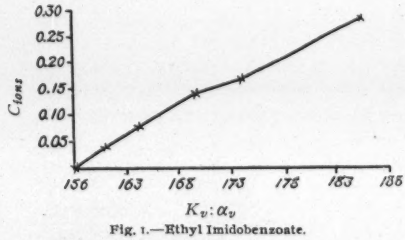

Fig. 1.—Ethyl Imidobenzoate.

[1] This value is hypothetical.

Judging by these results, we would decide that the decomposition of the hydrochloride of ethyl imidobenzoate by water proceeds with a velocity proportional to the concentration of the positive ion of the salt, and this velocity is accelerated by the influence of a "salt effect" which is proportionate to the concentration of the salt ions present.[1] This result is in perfect agreement with Stieglitz's theory of the catalysis of esters.

2. The Hydrochloride of Methyl Imidobenzoate.

In order to test the theory more fully, a series of experiments, exactly similar to those performed with the hydrochloride of ethyl imidobenzoate, was carried out with the corresponding salt of methyl imidobenzoate. The tables and the symbols employed correspond to those in the preceding part of the paper, as do also all the experimental details; no further discussion, therefore, is required.

[1] This conclusion has been confirmed by the extended investigations of Dr. Barnard.

The Hydrochloride of Methyl Imidobenzoate.

Table VIIIa.

$v = 20.$ $w = 25$ cc. Mean, 43430 $K_v = 236.$

t	0	30	60	90	120	150	255	285	315
$(C—x)$	10.93	9.40	7.63	6.72	5.71	4.81	2.80	2.61	1.85
43430 K_v	....	218	260	234	235	237	230	218	257

Table VIIIb.

$v = 20.$ $w = 25$ cc. Mean, 43430 $K_v = 235.$

t	0	30	60	90	120	225	255	285
$C(—x)$	8.10	6.90	5.67	5.51	4.35	2.39	2.07	1.85
43430 K_v	.....	232	258	(186)	225	235	233	225

Table IXa.

$v = 10.$ $w = 10$ cc. Mean, 43430 $K_v = 242.$

t	0	30	60	90	120	150	270	300	330
$(C—x)$	9.38	7.96	6.47	5.75	4.88	3.99	2.20	1.75	1.5
43430 K_v	....	238	(269)	236	237	247	233	243	236

The Hydrochloride of Methyl Imidobenzoate.

Table IXb.

v = 10. w = 10 cc. Mean, 43430 K_v = 246.

t	0	30	60	90	120	150	271	301	330
$(C-x)$	9.47	7.75	6.37	5.85	4.79	4.18	2.10	1.82	1.50
43430 K_v	....	(290)	(287)	233	247	236	235	283	241

Table Xa.

v = 5. w = 10 cc. Mean, 43430 K_v = 234.

t	0	30	60	90	120	210	240	255
$(C-x)$	16.46	13.95	11.97	9.81	7.93	5.43	4.61	4.23
43430 K_v	....	239	231	(249)	(264)	230	236	237

Table Xb.

v = 5. w = 10 cc. Mean, 43430 K_v = 231.

t	0	30	60	90	150	240	270	315
$(C-x)$	18.50	15.96	13.30	11.45	8.27	5.40	4.49	3.56
43430 K_v	....	(214)	239	232	231	224	228	227

The Hydrochloride of Methyl Imidobenzoate.

Table XI.

$v = 4$. $w = 5$ cc. Mean, 43430 K_v = 230.

t	0	30	60	90	255	270	285	300	315
$(C-x)$	12.24	10.43	8.85	7.59	3.13	2.99	2.70	2.53	2.36
43430 K_v	....	232	235	231	232	227	231	228	227

Table XIIa.

$v = 2$. $w = 5$ cc. Mean, 43430 K_v = 207.

t	0	30	60	75	120	150	270	300	330
$(C-x)$	23.37	20.33	17.61	15.75	13.29	11.20	6.47	5.50	4.85
43430 K_v	....	202	205	(222)	205	(213)	207	207	207

Table XIIb.

$v = 2$. $w = 5$ cc. Mean, 43430 K_v = 208.

t	0	30	60	105	120	150	300	330
$C-x$	23.89	20.70	17.66	14.46	13.43	11.32	5.76	4.99
43430 K_v	....	208	(218)	208	209	(216)	206	206

Table XIII.[1]*—The Degree of Ionization of the Hydrochloride of Methyl Imidobenzoate.*

1	2	3	4	5	6	7
V.	Λv.[2]	Δ.	$\Lambda\infty$.[2]	Λv.[3]	$\Lambda\infty$.[3]	$\alpha v \times 100$.
2	31.6	....	....	32.9	....	58.5
4	38.5	....	....	38.6	....	70.0
5	40.1	....	....	39.8	....	72.5
10	43.8	....	....	44.7	....	80.3
32	48.2	6.7	54.9	48.2	54.9	87.5
64	50.1	5.3	55.4	49.9	55.1	90.7
128	51.8	3.8	55.6	50.7	54.5	92.5
		Mean,	55.3	Mean,	54.9	

Average $\Lambda\infty$ = 55.1.

Table XIV.[4]

1	2	3	4	5	6
m.	$100\,\alpha v$.	$43430\,Kv$.	$43430\frac{Kv}{\alpha v}$.	$43430\,K_{calc.}$	$43430\,K'_{calc.}$
0.50	58.5	207	354	225	206
0.25	70.0	230	328	231	225
0.20	72.5	232	320	231	227
0.10	80.3	244	304	238	237
0.05	84.6[5]	236	279	242	242
0.05	84.6	242[6]	286[7]	242	242
0.00	....	...	275[7]	...	...

The values in the table above (Table XIV.) give the relations of the velocity of decomposition of the hydrochloride of the methyl imidobenzoate (as taken from Tables VIII.–XIII.) to the degree of ionization of the salt and to the "salt effect" in any concentration. In Table XIV., as in Table VII., column 3 gives the velocities actually observed (K_v), and in columns 5 and 6 the theoretical velocity constants

[1] Tables XIII. and XIV. are comparable to Tables VI. and VII., respectively.

[2] Column 2 contains Λv when N/80 base was used in excess. In column 4 the $\Lambda\infty$ was calculated from Λv in column 2.

[3] Column 5 contains Λv when N/40 base was used in excess; column 6, the corresponding $\Lambda\infty$.

[4] Tables XIII. and XIV. are comparable to Tables VI. and VII., respectively.

[5] Taken from the ethyl ester. See Table VI., column 7.

[6] Taken from the work of Derby: *Loc. cit.* Mean of 23 determinations.

[7] The acceleration due to salt is taken from these two values. It is $\frac{11.1}{275} = 0.04$ for 0.05 mole of salt.

as calculated by equations analogous to (10′) and (11′), respectively, are given;[1] into this last column "salt effect" and degree of ionization are both incorporated. It is noticeable at once that the calculated values ($K'_{calc.}$) for an accelerating effect of the salt *ions* agree remarkably well (within 2–3 per cent) with the observed velocities (K_v). As was expected, the values calculated for an accelerating effect proportional to the total salt ($K_{calc.}$) do not agree so well with the observed velocities—the maximum deviation being as high as 8.8 per cent in one case. In both cases, therefore, for the hydrochlorides of methyl as well as of ethyl imidobenzoate, the agreement between the velocities calculated on the basis of an equation like (11′) agree well with the observed velocities. We may consider then that such an equation actually gives the best expression of the course of the reaction according to which an imidoester salt is decomposed into an ester and an ammonium salt (equation 2′).[2]

PART II.

The Catalysis of Imidoesters by Means of the Hydroxyl Ion.

A qualitative investigation of the action of alkalis on imidoesters of the aromatic series showed that the reaction proceeds in a direction different from that exhibited in acid solution; instead of an ester and an ammonium salt (equation 2′), a nitrile and an alcohol are formed according to the equation

$$C_6H_5C(:NH)OR = C_6H_5C{\equiv}N + HOR \qquad (12).$$

This, it should be noted, is a reversal of the synthetic method of preparing imidoesters from nitriles and alcohols in the presence of acids.

The quantitative determinations of the velocity of decomposition, under the influence of varying proportions of barium hydoxide, show that the velocity is always directly proportional to the concentration of the imidoester and to the concentration of the hydroxyl ion, *i. e.*,

[1] The acceleration is taken as 4 per cent for 0.05 mole salt.

[2] Work is being continued along these lines by Mr. W. Hickman, velocities being measured at 0° as well as at 25°.—J. S.

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times C_{OH} \qquad (13).^1$$

The hydroxyl ion may be said to act "catalytically," in the old sense of the term, as it does not appear to be involved in the reaction and its concentration remains constant. This is true because both the original imidoester used and the alcohol formed are too weak acids to neutralize appreciably the alkali in the dilute solutions used. For a given experiment, therefore, we may write

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times k_{OH} \qquad (14),$$

$$= K_v \times C_{ester} \qquad (14').^1$$

Or $$\frac{dx}{dt} = K_v \times (C - x) \text{ and}$$

$$K_v = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (15).$$

The velocity constant of the decomposition, K_{OH}, is, according to (14) and (14'),

$$K_{OH} = \frac{K_v}{k_{OH}} \qquad (16),$$

in which k_{OH} is the given concentration of the hydroxyl ion used in an experiment and K_v is the observed velocity constant in that experiment. If the decomposition actually proceeds according to (13), the same value for K_{OH} ought to be obtained from all the determinations, independent of the concentration of the imidoester and of the barium hydroxide used. The results reported below fully prove that such is the case.

According to the theory developed in Stieglitz's paper,[2] the enormous acceleration of the decomposition of imidoesters into alcohols and nitriles produced by alkalis as catalytic agents must be due to acid properties of the imidoesters. Such a character would lead to the formation of metal salts

[1] C_{ester} is a function of x.
[2] *Loc. cit.*

whose *negative ion* would be the actual substance undergoing decomposition and the concentration of whose negative ion would constantly represent the real "active mass" at any moment. The imidoesters, consequently, must have an amphoteric character, ionizing chiefly as bases, yet minimally also as acids, and forming salts with the alkalis. There are two ways in which such a salt formation could occur; either by direct addition of alkali to the imidoester, just as to an ordinary ester,[1] according to the equation

$$C_6H_5C(:NH)OR + NaOH = C_6H_5\begin{cases}NH_2\\ ONa\\ OR\end{cases} \qquad (17),$$

or by salt formation in the imido group according to the equation

$$C_6H_5C(:NH)OR + NaOH = C_6H_5C(:NNa)OR + H_2O \quad (18).$$

In view of the fact that the very closely related class of bodies, the amidines, $RC(:NH)NH_2$, besides their pronounced basic properties—they are far stronger bases than the imido esters, even stronger than ammonia—have been shown to possess also weak acid properties, forming salts such as $RC(:NMe)NH_2$[2] and $RC(:NC_6H_5)(NMeC_6H_5)$,[3] it is extremely probable that equation (18) represents the actual method of salt formation.[4] For the further development of our theory, it is a matter of indifference whether (17) or (18) is correct, but (18) gives a rather more simple decomposition of the imidoester into nitrile and alcohol than does (17), from which one would expect the formation of an alcohol and an acid amide, $RCONH_2$.

The salts of very weak acids, as the imidoesters must be, are hydrolyzed in aqueous solutions according to the formulation

$$C_6H_5C(:NMe)OR + HOH \rightleftarrows C_6H_5(:NH)OR + MeOH \qquad (19),$$

[1] Claissen: Ber. d. chem. Ges., **20**, 641 (1887); Nef: Ann. Chem. (Liebig), **270**, 322; **287**, 279.

[2] Bruce: J. Am. Chem. Soc., **26**, 419 (1904).

[3] Bamberger: Ann. Chem. (Liebig), **273**, 277 (1893).

[4] The isolation and analysis of the metal salts of the imidoesters will be attempted in this laboratory.

and we would have for the *free weak acid* (the imidoester)

$$\frac{C_{neg.\,ion} \times C_H}{C_{mol.}} = k_{acid} \qquad (20),$$

in which the $C_{neg.\,ion}$ represents the concentration, in the usual units, of the negative ion of the acid, C_H the concentration of hydrogen ions, and $C_{mol.}$ that of the nonionized acid, and k_{acid} is the affinity (ionization) constant of the imidoester as an acid. The proportion of ester which is ionized as an acid is so exceedingly small that we may consider the concentration of the nonionized ester, $C_{mol.}$, equal to the total concentration of ester, C_{ester}, at any moment and hence write

$$\frac{C_{neg.\,ion} \times C_H}{C_{ester}} = k_{acid} \qquad (20').$$

Since

$$C_H \times C_{OH} = k_{H_2O} \qquad (21),$$

we have, combining (21) and (20'),

$$\frac{C_{neg.\,ion}}{C_{ester} \times C_{OH}} = \frac{k_{acid}}{k_{H_2O}} \qquad (22).$$

If, now, according to Stieglitz's theory, the substance which is actually undergoing decomposition into a nitrile and an alcohol is the negative ion of the imidoester, in other words, if we put simply

$$\frac{dx}{dt} = K_{ion} \times C_{neg.\,ion} \qquad (23),^1$$

then we must find the following equation, obtained by combining (23) and (22), to be true:

$$\frac{dx}{dt} = K_{ion} \times \frac{k_{acid}}{k_{H_2O}} \times C_{ester} \times C_{OH} \qquad (24),$$

$$= K_{OH} \times C_{ester} \times C_{OH} \qquad (25).$$

This expression, however, is identical with equation (13), which is, on the one hand, in perfect agreement with the experimental results; and can, on the other hand, it is seen, be deduced theoretically by the application of the well-known

[1] $C_{neg.\,ion}$ is a function of x.

laws of chemical equilibrium to the fundamental conception of salt and ion formation as the explanation of the catalytic action of acids and bases.

We may, therefore, properly write the decomposition reaction in alkaline solution as follows:

$$C_6H_5\diagdown\!\!\!\!\diagup \begin{matrix}\bar{N}\\ OR\end{matrix} = C_6H_5C\equiv N + \bar{O}R \qquad (26),$$

which corresponds in every way to equation (2′) for the decomposition of the positive imidoester ions into ammonium ions and esters. In the latter case, the basic properties of the imidoesters were sufficiently strong to permit a determination of the actual concentrations of the *positive* ion and of the real constant, K_{ion}; in the case of the decomposition of the *negative* ions into nitriles and alcohols, the acid ionization of the imidoester is so slight that the determination of k_{acid} in equations (20) and (22) was not attempted, and consequently we have been unable to resolve the experimental constant K_{OH} of equation (25). But from the fact that K_{OH} has been found to be 1.991 for methyl imidobenzoate (see below), it is seen that the velocity of decomposition of the negative ion is very much larger than the velocity of decomposition of the positive ion of the same ester, whose value has been found to be 0.0063 (see p. 737, Table XIV.). There again, the imidoesters show a perfect parallelism to the ordinary esters, which are decomposed very much faster by alkalis than by acids.

EXPERIMENTAL.

The qualitative examination of the change of the imidoesters in alkaline solution was made on two representative substances, methyl imidobenzoate and methyl imido-*m*-nitrobenzoate. The experiments were carried out as follows: About one gram of the ester was weighed out into a tube of about 50 cc. capacity and to this was added a measured amount of N/10 barium hydroxide. The tube was then attached to the wheel of a small engine and shaken for ten to twenty hours. In the case of the methyl imidobenzoate, benzoni-

trile separated out as a heavy oil; this was filtered off, dried in a desiccator, and weighed. In order to establish its identity, a portion was dissolved in alcohol, mixed with 15 drops of concentrated ammonia solution, and treated for sixty hours with hydrogen sulphide. The resulting thiobenzamid was dissolved in dilute sodium hydrate and reprecipitated by means of carbon dioxide. This product, when dry, melted at 115°. No very accurate quantitative results were obtained in this way in the case of methyl imidobenzoate, as benzonitrile is quite soluble in water and there is another loss; it was necessary to wash the filter with a few drops of alcohol, as was done with the tube in order to obtain all of the nitrile; the alcohol was completely evaporated in the desiccator, but experiment showed that benzonitrile was also slightly volatile under these circumstances. In spite of these difficulties, 0.9 gram of methyl imidobenzoate, when treated with 25 cc. of N/10 barium hydroxide, for twelve hours, yielded 0.35 gram of benzonitrile—50 per cent of the theoretical value. In the case of methyl imido-*m*-nitrobenzoate, the nitrile, under the treatment described, separated as a white, crystalline substance. It was filtered from the solution, washed with dilute hydrochloric acid to remove any unchanged solid ester, dried on a clay plate, and weighed. The nitrile thus obtained melted sharply at 116°. The filtrate was then heated to about 80° in the presence of dilute hydrochloric acid to convert any unchanged dissolved ester into methyl *m*-nitrobenzoate and extracted with low boiling ligroin. The extract was dried with calcium chloride and allowed to evaporate spontaneously. Only a small quantity of pure *m*-nitrobenzonitrile was left. One gram of ester shaken for 20 hours with 25 cc. of N/10 barium hydroxide yielded 0.5 gram of nitrile—67 per cent of the theoretical value. It is apparent, therefore, that equation (12) represents the chief reaction.

The quantitative study of the accelerating action of hydroxyl ions on the decomposition of imidoesters into nitrile and alcohols included velocity determinations on methyl, ethyl, propyl, and isopropyl imidobenzoates and methyl imido-*m*-nitrobenzoate. The method of analysis used to follow the reac-

tion and the conditions of the experiment will be described in detail for the first one of the series examined, methyl imidobenzoate, where special precautions had to be used.

1. Methyl Imidobenzoate.

Methyl imidobenzoate was prepared from its hydrochloride by treatment of the latter with three times the calculated amount of a cold 30 per cent solution of sodium hydroxide and rapid extraction with ether. The extract was dried with calcium chloride and the ether distilled off under diminished pressure. The remaining oil was then distilled at a pressure of 2 mm. or less.[1] At this pressure, methyl imidobenzoate (as well as ethyl, propyl, isopropyl, and isobutyl esters) distil without visibly boiling and without decomposition. In order to test the purity of the compound, it was titrated[2] with N/10 hydrochloric acid. Instead of stopping the addition of acid at the ordinary "neutral" tint, the solution was titrated to a "standard" tint prepared by adding a few drops of the indicator (methyl orange) to a N/50 solution of corresponding pure hydrochloride. The ester was diluted so as to give, when titrated, a salt solution of the same concentration as that of the standard tint. The very slight hydrolysis of the hydrochloride is by this means prevented from affecting the accuracy of the titrations.

The velocity of decomposition of the imidoesters in the presence of barium hydroxide was determined, as in the case of the hydrochlorides, at 25° (±0°.01). The required amount of N/10 barium hydroxide was run into a 500 cc. graduated flask and the solution made up to the mark. This aqueous solution was poured into an ordinary 750 cc. flask and kept, well stoppered, in the bath until it had acquired the proper temperature. The ester was kept in a weighing bottle which contained a little pipette; in this way it was possible to weigh out the ester directly into the solution of barium hydroxide. Errors in volume introduced by this method were found to be negligible. The greatest difficulty, however, lay in find-

[1] A mercury pump was employed.

[2] The titration was carried out in Nessler tubes.

ing a means of analysis by which to follow the course of the reaction. Finally, a simple method was adopted. A measured amount of solution was run, by means of a calibrated pipette, into an Erlenmeyer flask and titrated with N/10 hydrochloric acid. Alizarin sulphonate was used as indicator since no sharp "end point" could be determined with methyl orange. Even with this delicate indicator considerable difficulty was experienced; this was true especially at the beginning of the reaction where the concentration of the imidoester relative to the amount of barium hydroxide was fairly large, and where a very small error in titration markedly affects the constant. The calculation of the amount of unchanged ester from these titrations is very simple. Experiment showed that the reaction products contained in the solution do not affect the titration. Thus barium hydroxide could be sharply titrated in the presence of benzamide, which might be formed to some extent by the action of baryta on the first reaction product, benzonitrile; it could likewise be titrated in the presence of benzonitrile and of both compounds at the same time. The neutral tint, when it was once obtained, did not change for several hours. Therefore the amount of acid used in titrating the measured amount of solution represents the total base contained in the given volume; subtracting from this the acid required for the known amount of barium hydroxide, we have, as the remainder, the concentration of unchanged ester. In Tables XV.–XIX. these values are placed in line 2, following $(C-x)$.

The amount used for each titration is 50 cc., unless otherwise stated under w; the amount of barium hydroxide contained in the volume titrated is given under ba; the time in minutes is given in line 1, and the velocity constant calculated from equation (15) in line 3. The concentration of ester for each benzoate is approximately the same throughout the series of tables; its value appears in the equation as $(C-x)$ and is given in terms of N/10 alkali.

Methyl Imidobenzoate.

Table XVa.

w = 50 cc. ba = 0.59. Mean, 43430 K_v = 102.

t	0	20	60	80	100	120	140	160
$C-x$	6.60	6.27	5.63	5.44	5.18	5.00	4.78	4.54
K_v	....	(111)	(115)	105	105	100	100	101

Table XVb.

ba = 0.58. Mean, 43430 K_v = 100.

t	0	20	40	60	80	100	120	140	160
$C-x$	5.94	5.66	5.32	5.18	4.88	4.69	4.54	4.34	4.19
K_v	....	105	120	99	107	103	97	97	95

Table XVIa.

ba = 1.14. Mean, 43.430 K_v = 193.

t	0	20	41	60	80	100	120	140	160	180
$C-x$	6.56	5.91	5.33	4.93	4.52	4.21	3.84	3.64	3.31	3.03
K_v	....	(227)	(220)	208	202	193	194	182	188	186

Table XVIb.

ba = 1.20. Mean, 43430 K_v = 203.

t	0	42	60.5	80	100	120	140	160
$C-x$	6.37	5.19	4.72	4.40	4.01	3.64	3.27	3.00
K_v	....	(211)	(215)	201	201	202	207	204

Methyl Imidobenzoate.

Table XVIIa.

ba = 3.18. Mean, 43430 K_v = 511.

t	0	21	40	60	80	100	120	140	160	180
$C-x$	5.33	4.17	3.33	2.68	2.18	1.66	1.29	1.02	0.80	0.61
K_v	....	....	500	510	497	485	513	512	514	543

Table XVIIb.

ba = 3.11. Mean, 43430 K_v = 497.

t	0	20	42	60	80	100	120	140	160	180
$C-x$	5.47	4.37	3.42	2.76	2.10	1.77	1.37	1.13	0.84	0.65
K_v	....	(487)	(489)	495	519	490	501	488	501	514

Table XVIIIa.

ba = 4.66. Mean, 43430 K_v = 742.

t	0	11	20	30	42	50	60.5	70	80
$C-x$	6.40	5.31	4.62	3.90	3.09	2.72	2.33	1.96	1.63
K_v	....	736	(707)	(702)	753	743	(725)	734	743

Table XVIIIb.

ba = 4.80. Mean, 43430 K_v = 741.

t	0	10	20	30	40	50	61	70	80
$C-x$	6.37	5.41	4.55	3.80	3.25	2.71	2.24	1.92	1.56
K_v	....	(703)	(723)	745	(729)	741	743	743	(764)

Methyl Imidobenzoate.

Table XIXa.

ba = 7.02. Mean, 43430 K_v = 1090.

t	0.0	10	20	30	40	47	55	62.5	70
$C—x$	5.82	4.58	3.52	2.73	2.07	1.84	1.39	1.17	0.89
K_v	....	1040	1090	1100	1120	1070	1130	1110	1110

Table XIXb.

ba = 7.06. Mean, 43430 K_v = 1090.

t	0.0	10	20	30	40	48	55	63	70
$C—x$	6.16	4.79	3.74	2.85	2.22	1.82	1.58	1.26	0.99
K_v	....	1090	1080	1120	1110	1100	1070	1090	1130

From the data found in these tables it can be shown that the velocity of the decomposition of methyl imidobenzoate in alkaline solution is proportional to the concentration of the hydroxyl ion,

$$K_v = K_{OH} \times C_{OH} \text{ and } K_{OH} = \frac{K_v}{C_{OH}},$$

in which K_v is the observed velocity constant and C_{OH} the concentration of the hydroxyl ion in a given series. C_{OH}[1] is determined from the concentration of the barium hydroxide used and its known degree of dissociation as calculated from its conductivities.[2] The values obtained in this way will be found in Table XX. In column 1 the number of the experiment is given, in column 2 will be found the amount of N/10 barium hydroxide used in 500 cc. of solution, in column 3 the corresponding degree of ionization of the barium hydroxide, in column 4 the concentration of the hydroxyl ion for each cubic centimeter of solution; column 5 contains the observed velocities, K_v, and column 6 this value divided by the hydroxyl concentrations.

Table XX.

1	2	3	4	5	6
No.	$Ba(OH)_2$.	100 α_v.	$10^5 \times (OH)$.	43430 K_v.	0.434 $\times K_{OH}$.
XVa	5.90	97.5	115	102	0.887
XVb	5.80	97.5	113	100	0.885
XVIa	11.40	97	221	193	0.873
XVIb	12.00	97	233	203	0.871
XVIIa	31.80	96	610	511	0.837
XVIIb	31.10	96	597	497	0.833
XVIIIa	46.60	95	886	742	0.840
XVIIIb	48.00	95	912	741	(0.812)
XIXa	70.20	93	1306	1090	0.835
XIXb	70.60	93	1313	1090	0.830

Mean, 0.4343 $K_{OH} = 0.854$. $K_{OH} = \frac{0.854}{0.4343} = 1.97$.

[1] Neglecting the OH ions due to the ester itself. This is exceedingly small in comparison with the OH ions from barium hydroxide since the ionization of a weak base is suppressed by the presence of a strong base.

[2] Kohlrausch and Holbein: "Leitvermögen der Electrolyte," p. 167.

The values in Table XX. for K_{OH} indicate that the hypothesis regarding the proportionality between the velocity of decomposition and the hydroxyl concentration is a correct representation of the facts. Below will be found similarly conclusive evidence in the case of the other esters investigated.

2. Ethyl Imidobenzoate.

Tables XXI.–XXIII. give the velocity determinations. In these everything corresponds to the work on the methyl ester. All the solutions were made up to 500 cc. and 50 cc. was used for each titration. The symbols used have the same significance as in the case of the methyl ester.

Ethyl Imidobenzoate.

Table XXIa.

ba = 3·59. Mean, 43430 K_v = 205.

t	0	21	40	60	80	100	120	140	160
$C-x$	5·87	5·33	5·30	4·38	4·06	3·66	3·34	3·00	2·70
K_v	....	199	(110)	210	200	205	204	208	211

Table XXIb.

ba = 3·57. Mean, 43430 K_v = 204.

t	0	20	65	85	105	125	145	165
$C-x$	6·89	6·25	5·14	4·64	4·17	3·84	3·47	3·13
K_v	....	212	195	202	208	202	205	207

Table XXIIa.

ba = 5·22. Mean, 43430 K_v = 299.

t	0	25	35	45	65	85	105	125	145	165
$C-x$	5·88	4·90	4·76	4·23	3·81	3·29	2·85	2·49	2·18	1·89
K_v	....	317	(268)	318	290	296	300	300	298	299

Table XXIIb.

ba = 5.35. Mean, 43430 K_v = 310.

t	0	25	40	50	90	110	130	150	175
$C-x$	6.22	6.08	4.64	4.40	3.27	2.85	2.47	2.07	1.78
K_v	....	(40)	318	301	310	311	308	317	311

Table XXIIIa.

ba = 7.01. Mean, 43430 K_v = 401.

t	0	15	30	45	55	65	75	86	100
$C-x$	6.40	5.58	4.82	4.20	3.87	3.54	3.19	2.90	2.57
K_v	....	398	410	407	397	403	403	400	396

Table XXIIIb.

ba = 7.04. Mean, 43430 K_v = 401.

t	0	25	75	85	110	130	150	175	190
$C-x$	6.16	4.90	3.06	2.83	2.25	1.79	1.56	1.11	0.80
K_v	....	395	404	399	397	412	394	(425)	(466)

Table XXIV.

1 No.	2 $Ba(OH)_2$.	3 $100\alpha_v$.	4 $10^5\times(OH)$.	5 $43430\,K_v$.	6 $0.4343\times K_{OH}$.
XXIa	35.90	96	689	205	0.298
XXIb	35.70	96	685	202	0.298
XXIIa	52.20	95	992	299	0.301
XXIIb	53.50	95	1070	310	0.290
XXIIIa	70.10	93	(1304)	401	0.307
XXIIIb	70.40	93	(1309)	402	0.307

Mean, $0.43430\,K_v = 0.300$. $K_{OH} = \dfrac{0.300}{0.4343} = 0.69$.

It is evident that the agreement between theory and experiment is as good for the ethyl ester as it is for the methyl ester.

3. n-Propyl Imidobenzoate.

Tables XXV.–XXVII. contain the velocity determinations. The solutions in each case were made up to 500 cc. and 50 cc. was used for each titration.

Table XXVa.

ba = 3.05. Mean, 43430 K_v = 152.

t	0	15	30	50	70	90	130	150	170
$C-x$	3.19	3.03	2.84	2.63	2.47	2.39	1.99	1.88	1.77
K_v	....	150	(170)	(168)	160	144	160	153	150

Table XXVb.

ba = 3.07. Mean, 43430 K_v = 171.

t	0	20	40	60	70	80	100	120	140
$C-x$	3.38	3.16	2.86	2.62	2.51	2.46	2.29	2.14	2.03
K_v	....	146	181	184	185	172	169	174	160

Table XXVIa.

ba = 6.15. Mean, 43430 K_v = 255.

t	0	20	40	60	80	100	120	140	160
$C-x$	3.65	3.29	2.90	2.48	2.27	1.91	1.84	1.64	1.38
K_v	....	226	250	270	258	281	240	250	264

Table XXVIb.

ba = 6.43. Mean, 43430 K_v = 291.

t	0	20	40	60	80	100	120	140	160
$C-x$	3.25	2.72	2.38	2.17	1.92	1.70	1.43	1.28	1.08
K_v	....	(387)	(340)	292	286	281	300	290	298

Table XXVIIa.

ba = 4.56. Mean, 43430 K_v = 207.

t	0	20	40	60	80	100	120	141	160
$C-x$	3.35	2.95	2.74	2.50	2.27	2.13	1.89	1.76	1.55
K_v	....	(276)	218	211	210	197	207	200	209

Table XXVIIb.

ba = 4.62. Mean, 43430 K_v = 210.

t	0	20	40	60	80	100	120	140	160
$C-x$	3.28	2.98	2.57	2.47	2.19	1.99	1.80	1.66	1.47
K_v	....	208	222	205	194	217	217	201	218

Table XXVIII.

1 No.	2 $Ba(OH)_2$.	3 $100\,\alpha_v$.	4 $10^5 \times (OH)$.	5 $43430\,K_v$.	6 $0.4343 \times K_{OH}$.
XXVa	30.50	96	591	152	0.255
XXVb	30.70	96	596	171	(0.285)
XXVIa	61.50	94	1156	255	0.220
XXVIb	64.30	94	1208	291	0.241
XXVIIa	45.60	95	866	207	0.239
XXVIIb	46.20	95	878	210	0.239

Mean, 0.4343 $K_{OH} = 0.239$. $K_{OH} = 0.55$.

4. Isopropyl Imidobenzoate.

Tables XXIX.–XXXI. contain the velocity determinations. The solutions in each case were made up to 500 cc. and 50 cc. was used for each titration.

Table XXIXa.

ba = 3.09. Mean, 43430 K_v = 67.6.

t	0	20	30	40	60	80	100	120	156
$C-x$	4.96	4.79	4.73	4.67	4.50	4.34	4.28	4.14	3.90
K_v	....	(75.2)	68.4	65.4	70.4	72.4	64.0	65.4	67.5

Table XXIXb.

ba = 3.22. Mean, 43430 K_v = 67.5.

t	0	40	60	80	100	141	162	175	190
$C-x$	4.97	4.55	4.38	4.27	4.11	3.91	3.77	3.71	3.63
K_v[1]	....	....	(82.0)	69.0	73.6	65.1	66.9	64.9	65.4

Table XXXa.

ba = 4.62. Mean, 43430 K_v = 101.

t	0	20	40	60	80	100	120	140	160
$C-x$	4.69	4.48	4.23	4.11	3.93	3.68	3.59	3.39	3.18
K_v	....	100	112	96	96	105	97	101	105

[1] Calculated from $t = 40$, $1 - x = 4.55$.

Table XXXb.

ba = 4.65. Mean, 43430 K_v = 109.

t	0	21	40	60	80	100	120	140	160
$C-x$	4.82	4.55	4.29	4.14	3.94	3.75	3.59	3.46	3.22
K_v	....	115	(126)	110	109	109	107	103	110

Table XXXIa.

ba = 6.10. Mean, 43430 K_v = 130.

t	0	23	42	60	80	100	120	140	160
$C-x$	4.54	4.15	3.93	3.78	3.50	3.40	3.16	2.99	2.84
K_v	....	(170)	(150)	133	141	126	131	130	127

Table XXXIb.

ba = 6.16. Mean, 43430 K_v = 128.

t	0	23	41	60	80	101	120	140	160
$C-x$	4.26	3.92	3.63	3.58	3.36	3.14	3.01	2.88	2.63
K_v	....	(160)	(170)	130	131	127	126	122	131

Table XXXII.

1 No.	2 $Ba(OH)_2$.	3 $100\alpha_v$.	4 $10^4\times(OH)$.	5 $43430\times K_v$.	6 $0.4343\times K_{OH}$.
XXIXa	30.90	96	593	67.6	0.114
XXIXb	32.20	96	618	67.5	0.109
XXXa	46.20	95	878	101	0.115
XXXb	46.50	95	884	109	0.123
XXXIa	61.50	94	1156	130	0.113
XXXIb	61.60	94	1158	128	0.111

Mean, $0.4343\ K_{OH} = 0.114$. $K_{OH} = 0.265$.

5. Methyl Imido-m-nitrobenzoate.

Methyl imido-*m*-nitrobenzoate was prepared from its hydrochloride by treating this with three times the required amount of a cold 30 per cent solution of sodium hydroxide and rapidly extracting the base with ether. The extract was dried and the ether evaporated at reduced pressure, leaving the ester behind as a yellow solid. Upon crystallization from low boiling ligroin, this was obtained as a white, crystalline substance melting at 53°. Dissolved in hydrochloric acid and heated, it yielded *m*-nitrobenzoic methyl ester, melting at 70°. On account of the slight solubility of the ester in water, one liter of a N/200 solution was made up for each velocity determination, and 100 cc. were used for each titration. It was impossible to titrate these solutions in the ordinary way; the lack of a sharp change of tint, even with the help of alizarin sulphonate, made it necessary to titrate in Nessler tubes, using as a standard tint for the end point of the reaction a faintly alkaline solution of alizarin sulphonate. Even under these conditions considerable difficulty was experienced in making the titrations at the beginning of the reaction. The indistinct color change, mentioned above,[1] is not the only difficulty. In the case of the nitrobenzoate a brownish compound seems to be formed as a result of an action of the ester on the indicator. The formation of this substance produces a color change similar to that produced by making the acid solution alkaline, and only by very rapid titration could the confusion resulting from this secondary reaction be avoided. Below are given the results of the velocity reactions; the symbols have the same significance as in the previous experiments.

[1] Page 745.

Table XXXIII.

ba = 3.27. Mean, 43430 K_v = 510.

t	0	19	33	59	70	83	100	115
$C-x$	2.57	2.08	1.86	1.31	1.17	1.01	0.79	0.64
K_v	....	500	(440)	500	500	500	520	530

Table XXXIV.

ba = 4.37. Mean, 43430 K_v = 690.

t	0	12	22	34	42	55	66	80	88
$C-x$	2.32	1.92	1.68	1.35	1.15	0.89	0.78	0.65	0.46
K_v	....	680	640	690	700	(750)	720	690	(790)

Table XXXV.

ba = 6.25. Mean, 43430 K_v = 930.

t	0	20	34	65	75	88	100	110
$C-x$	3.50	2.23	1.55	0.91	0.73	0.57	0.35	0.25
K_v	....							

Table XXXVI.

1 No.	2 $Ba(OH)_2$.[1]	3 100 α.	4 $10^5 \times (OH)$.	5 43430 K_v.	6 0.4343 K_{OH}.
XXXIII	32.70	96	314	510	1.62
XXXIV	43.70	95	415	690	1.66
XXXV	62.50	96	600	930	1.55

Mean, 0.4343 K_{OH} = 1.61. K_{OH} = 3.7.

PART III.

The Velocity of Decomposition of Imidoesters in Aqueous Solution.

Besides the study of the velocity of decomposition of imidoesters under the influence of added acids or alkalis, an investigation of the velocity of decomposition of methyl imidobenzoate in aqueous solution was undertaken, since only a few preliminary determinations had been carried out by Derby.[2] The experimental results are given below; they agree perfectly with the preliminary determinations just mentioned. The theoretical interpretations which should be placed on these results is a question of peculiar interest. Qualitatively, the chief reaction[3] in aqueous solution has been found to be the same as in alkaline solutions—a nitrile and an alcohol are formed. Quantitatively, the velocity determinations of the decomposition gave a constant according to the simple logarithmic function,

$$k_{ester} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (27).$$

This is the equation for a monomolecular reaction which proceeds proportionately to the concentration of the total substance.

In an aqueous solution of a substance like methyl imidobenzoate, which is a very weak base and also, as shown in Part II., a still weaker acid, we must have both its positive and its negative ions. Since these ions will be present only in very small amounts, practically all of the imidoester must be

[1] Column 2 represents in this table the cc. N/10 $Ba(OH)_2$ in 1 liter of the mixture.
[2] This Journal, **39**, 471.
[3] It is likely that an acid amide is to a small extent formed in a parallel reaction.

in the nonionized form. Calculations made with the aid of the affinity constant for the base as determined by Derby[1] show that in one-twentieth molar solution about 0.03 per cent of the free base is ionized and in one-hundredth molar solution less than 0.1 per cent is ionized. It is clear, therefore, that the concentration of the nonionized molecule may be put equal to the concentration of the total substance; and that consequently the constant obtained by the logarithmic function (27) would be the true constant giving the velocity of the reaction if the nonionized molecule forms the chief reacting substance in these solutions and breaks down into a nitrile and alcohol according to the equation

$$C_6H_5C(:NH)OCH_3 = C_6H_5C{:}N + HOCH_3 \qquad (28).$$

It should be noted that although the products in this reaction are also ultimately a nitrile and an alcohol, as in strongly alkaline solutions, the reaction equations in the two cases are different. In the latter instance, we have the reaction expressed by equation (26),[2] which shows that the negative ions are breaking down into nitriles and alcohol ions ($\overline{OR}$). As was to be expected, the characteristic velocity constants for the two different reactions are different. K_{OH}, the velocity constant for the decomposition of the negative ion when one gram molecule of ester is acted upon by one gram ion of hydroxyl was found to be 1.97 for methyl imidobenzoate, and K_{ester}, the constant calculated from (27), according to which the nonionized molecule breaks down, is only 0.00028. So even if both the negative ions and the nonionized imidoesters should give qualitatively the same ultimate products, it is obvious that the negative ions are by far the more reactive constituents in the solution; and, therefore, the rate of change of the nonionized molecules would become of moment only when, by an enormous advantage in concentration, their decomposition becomes the fundamental one. This view, of course, is the simplest possible one based on the fact that the velocity of the decomposition of the methyl imidoben-

[1] *Loc. cit.*
[2] P. 742.

zoate in aqueous solution is found to be determined by the logarithmic equation (27).

Before accepting this view, however, of the decomposition of the nonionized molecule, we shall also consider the fact that both the positive and the negative ions which must be present in the solution must also be decomposing as established in Parts I. and II., and we shall try to determine whether, small as their concentrations are, their relatively very great rates of decomposition cannot account for the actual velocity of decomposition observed in aqueous solution.

Since the decomposition constant for the negative ion is very much larger than for the positive imidoester ion, and since the aqueous solution of the free base is strongly alkaline, we might very well have a case of auto-catalysis in which the reaction proceeds exactly as in the presence of hydroxyl ions from barium hydroxide. On this account we shall first consider whether the observed velocity of decomposition can be accounted for as due simply to the decomposition of the imidoester under the influence of the hydroxyl ions produced from itself. The fundamental equation which would apply to such a reaction is

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times C_{OH} \qquad (13).$$

Whereas in the presence of barium hydroxide C_{OH} is a constant throughout the course of the experiment and variable only by way of different original concentrations of the hydroxide, in the case under discussion C_{OH} is a variable depending on the concentration of the reacting ester itself. There are two possibilities to be considered in endeavoring to establish the nature of this dependence. First, the concentration of the hydroxyl ion at any moment could be taken as dependent essentially on the ionization of the imidoester as a base alone, on the assumption that the acid character of the imidoester is so exceedingly weak that formation of more positive ions from a salt —which in turn would effect the concentration of the hydroxyl ion—would be so slight as to be negligible in the application of the general equation

$$\frac{C_{pos.\,ion} \times C_{OH}}{C_{mol.}} = K_{aff.} \qquad (29).$$

On this assumption we would obtain a *maximum* concentration of the hydroxyl ions to be used in connection with equation (13), and this is quite sufficient for our purpose. On the basis of such an assumption,

$$C_{OH} = \sqrt{K_{aff.} \times C_{mol.}},$$

and putting $C_{mol.} = C_{ester}$ we have

$$C_{OH} = \sqrt{K_{aff.} \times C_{ester}} \qquad (30).$$

Combining (30) and (13), we find

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times \sqrt{K_{aff.} \times C_{ester}},$$

$$= K_{OH} \times (C - x) \times \sqrt{K_{aff.} \times (C - x)} \qquad (31).$$

This, on integration, becomes

$$K_{OH} = \frac{2}{t_2 - t_1} \sqrt{\frac{1}{K_{aff.}}} \left\{ \frac{1}{(C - x_2)^{1/2}} - \frac{1}{(C - x_1)^{1/2}} \right\} \qquad (32).$$

The values for K_{OH}, calculated according to this equation (32), gave, indeed, a tolerably good constant for the whole course of each individual experiment carried on through a period of from seventy to eighty hours for each concentration; they did not, however, give the same constant for the varying original dilutions of the ester; and the constants were all *very much larger than the same constant*, K_{OH}, determined for the same ester by the action of barium hydroxide, as given in Part II.

In the following table, the first line, after V, gives the volume in liters containing a gram molecule of the free imido-ester; the second line, after $K_{mol.}$, gives the constant calculated according to equation (27), referring the active mass of the changing substance to the nonionized molecule, and the third line, after K_{OH}, gives the average constants calculated according to (32), on the assumption that the reaction in aqueous solution is a case of auto-catalysis, the hydroxyl

ion of the free base catalyzing the ester in the same way as barium hydroxide does.

Table XXXVII.

V	21.7	47.0	83.3	125
$K_{mol.}$	0.00028	0.00026	0.00026	0.00024
K_{OH}	22.6	30.1	40.7	45.2

The constant K_{OH} obtained in alkaline solutions by the addition of varying amounts of barium hydroxide to the aqueous solution of the free base is 1.97 (see p. 749, Table XX.). Since K_{OH}, as determined for the pure aqueous solution, is very much larger[1] than 1.97 and is not a constant for different dilutions, we are led to the conclusion that the reaction is not a case of auto-catalysis and that the chief reacting substance must be the nonionized molecule of the free base, breaking down, very slowly but with a constant velocity, in the course of seventy hours, into nitrile and alcohol. The important point in this conclusion is the fact that, having established in Parts I. and II. that both the positive and the negative ions of the imidoesters show characteristic, specific reactions proceeding with constant velocities, we now find that the third form of the esters, the nonionized form, also is active, changing exceedingly slowly, compared with the other forms, but with a measurable velocity[2] according to the equation

$$C_6H_5(:NH)OR = C_6H_5C{:}N + HOR \qquad (33).$$

In this calculation of C_{OH}, it will be recalled, the salt formation between the acid and the basic parts of the amphoteric was considered negligible (in equation 29). This was done because the basic functions are far more pronounced than the acid functions, as is shown by the marked alkaline reaction of the ester's aqueous solution. Taking the amphoteric character of imidoesters into account, we would have the case of

[1] The calculation was made on the assumption of a *maximum* possible concentration of OH ions (equation 29, p. 764), and K_{OH} would be still larger if the concentration of the OH ion were smaller, consequently the conclusions drawn in the text hold independently of this assumption.

[2] The importance of this question of the decomposition of the nonionized molecule is such that Mr. B. B. Freud will continue this part of the investigation to develop a broader range of experiments.—J. STIEGLITZ.

salt formation between a weak base and a very weak acid. Consequent hydrolysis of the salt would establish the condition of equilibrium expressed by the formulation

$$\underset{\text{base}}{C_6H_5C(NH)OCH_3} + \underset{\text{acid}}{C_6H_5C(:NH)OCH_3} \rightleftarrows [C_6H_5C(:NH)OCH_3]_2 \qquad (33).$$

Salt and acid formation take place, of course, at the imide (:NH) group in the molecule. In such solutions, we would have for the very weak acid:

$$\frac{C_H \times C_{neg.\ ion}}{C_{ester}} = k_{acid} \qquad (34),^1$$

and for the weak base

$$\frac{C_{OH} \times C_{pos.\ ion}}{C_{ester}} = k_{base} \qquad (35).^1$$

Combining (34) and (35), we have, as usual, for the hydrolysis of salts of weak acids and weak bases,

$$\frac{C_{neg.\ ion} \times C_{pos.\ ion}}{C^2_{ester}} = \frac{k_{acid} \times k_{base}}{k_{H_2O}} = k \qquad (36).$$

If the positive and negative ions are formed chiefly from the salt, as in the case of aniline acetate,[1] we may consider

$$C_{neg.\ ions} = C_{pos.\ ions},$$

and we would have

$$\frac{C^2_{neg.\ ion}}{C^2_{ester}} = K \qquad (37),$$

$$C_{neg.\ ions} = k' C_{ester} \qquad (37').$$

In a word, if salt formation does occur in the case of such an amphoteric substance, which is a weak base and a weak acid, to an extent such as to make the salt, rather than the base or acid, the chief source of the ions of the organic compound, then the concentration of the negative ions would be in practically constant proportion to the concentration of the total ester. Therefore, a reaction proceeding at a rate proportionate

[1] The concentration of the nonionized molecule may be put equal to that of the ester.

[2] Arrhenius: Z. physik. Chem., **5**, 19 (1890).

to the total ester would proceed also proportionately to the concentration of the negative ion. The reaction might also, on this account, be a function of the concentration of the negative ion, considered as the "active mass." This possibility is actually realized in the experimental results for the decomposition of methyl imidobenzoate in water solution —the rate of change is actually proportional to the total ester. This result in itself has justified us, in the study of the theory of the case, in not being content with only the first conclusion, *viz.*, that the nonionized imidoester *must* constitute the decomposing "active mass."

It will be recalled also that the fundamental equation,

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times C_{OH} \qquad (13),$$

is the experimental equation, identical with the one based on the theory of catalysis in alkaline solution, according to which negative ions represent the decomposing substance. This latter equation was written

$$\frac{dx}{dt} = K_{ion} \times C_{neg.\ ion} \qquad (23).$$

Theoretically, therefore, a reaction proceeding with a velocity directly proportional to the concentration of the total ester could be satisfied also by a constant representing the rate of change as proportional to the concentration of the negative ion of the *amphoteric* substance (equation 37′). The only question to be answered for the substance under investigation is whether the actual rate of change, as experimentally determined, agrees in value with that deduced from theory. This test may be made as follows:

Above it was shown that on the basis of an assumption that C_{OH} has a maximum value, the decomposition in aqueous solution is far too rapid to be cousidered a case of auto-catalysis. On the present assumption that the concentration of the positive ester ion is perceptibly increased by salt formation, C_{OH} (equation 29) and consequently also $C_{neg.\ ion}$ (equation 22)[1] must have still smaller values: the reaction ought to proceed

[1] This was established in Part II. and the whole argument rests on that work.

more slowly and this would be in still greater discrepancy with the experimental fact.

We are obliged to conclude again, therefore, that in aqueous solution methyl imidobenzoate decomposes into nitrile and alcohol with a speed too great to be accounted for on the assumption that it is proportional to the concentration only of the negative ion, as was found to be the case in strongly alkaline solutions.

The decomposition, which occurs simultaneously with that of the negative ion, of the positive ion into ammonia and ester (Part I.) is far too slow, in the minimal concentrations in which it is present, to account for this excessive speed. The velocity constant for that change is 0.0063 for methyl imidobenzoate (see Part I., p. 737, Table XIV., column 4). For a twentieth molar solution, the original concentration of the positive ion calculated from the affinity constant,

$$C^2_{ions} = 0.5 \times 10^{-8} \times C_{mol.},$$

is

$$C_{ion} = 0.000015.$$

The original rate of change of the ion referred to a whole gram molecule of the ester would be

$$0.000015 \times 0.006 \times 20 = 0.0000018,$$

a quantity which is negligible in accounting for the observed rate of change of one gram molecule total substance, *viz.*, 0.00028.[1]

EXPERIMENTAL.

The analytical method of following the decomposition of methyl imidobenzoate in aqueous solution was practically the one employed for the study of the decomposition of the same substance in strongly alkaline solution (see p. 745). Since the reaction proceeded very slowly, titrations were made at long intervals and special care was taken that no variations should occur in the temperature, the bath being kept at 25° (±0°.01) for several days. The logarithmic equation

[1] Only traces of ammonia and ester are formed, as a matter of fact.

(27) was used for obtaining the constants, $K_{mol.}$, given in the third columns of the following table, and equation (32) was used for the determinations of the values of K_{OH} (the fourth column). For these calculations, equation (32) is best transformed as follows: Calling the original concentration of the base 1 gram molecule in V liters and x_t the part of a gram molecule changed in t minutes, we have:

$$C = \frac{1}{V} \text{ and } C - x = \frac{1 - x'}{V}.$$

If v_o cc. and v_t cc. acid were used to neutralize the free base present in a measured amount of solution when $t = o$ and $t = t$ (*e.* g., 4.62 cc. and 4.34 cc., in Table XXXVIII., when $t = o$ and $t = 288$), then the unconsumed part, $(1 - x_t)$, of the free base may be expressed by

$$1 - x_t = \frac{v_t}{v_o}.$$

Equation (32) acquires the very simple form:

$$K_{OH} = \frac{2}{t}\sqrt{\frac{V}{K_{aff.}}}\left\{\sqrt{\frac{v_o}{v_t}} - 1\right\} \qquad (32').$$

Column 1, in the following tables, gives the time in minutes; column 2, the number of cc. 0.1 normal acid required to neutralize w cc. of the solution.

Table XXXVIII.

$V = 21.7$. $w = 10$ cc.

$t.$	$v_t.$	$43430\,K_{mol.}$	$K_{OH.}$	$t.$	$v_t.$	$43430\,K_{mol.}$	$K_{OH.}$
0	4.62	....	....	1963	2.60	12.7	22.6
288	4.34	(9.0)	(14.6)	2948	2.01	12.7	23.2
338	4.18	12.8	20.3	3169	1.80	12.9	25.2
438	4.13	11.1	17.5	3360	1.76	12.4	24.6
1521	3.00	12.3	21.0	4290	1.44	11.8	24.5
1684	2.88	12.2	20.9	4635	1.33	11.8	23.7

Mean, $K_{mol.} = 0.00028$. Mean, $K_{OH} = 22.4$.

Table XXXIX.

$V = 47$.				$w = 10$ cc.			
t.	vt.	43430 $K_{mol.}$	K_{OH}.	t.	vt.	43430 $K_{mol.}$	K_{OH}.
0	2.13	....	....	1935	1.24	12.0	31.1
266	1.92	(17.0)	(37.4)	2826	1.08	10.4	25.8
414	1.87	(13.6)	31.7	3143	0.99	10.6	29.5
1498	1.46	11.0	27.1	3338	0.90	11.2	31.5
1660	1.39	11.1	28.0	4265	0.69	11.4	34.7
1765	1.36	11.0	27.9	4553	0.67	11.0	33.7

Mean, $K_{mol.} = 0.00026$. Mean, $K_{OH} = 30.1$.

Table XL.

$V = 83.3$.				$w = 25$ cc.			
t.	vt.	43430 $K_{mol.}$	K_{OH}.	t.	vt.	43430 $K_{mol.}$	K_{OH}.
0	3.00	....	....	1926	1.80	11.5	39.3
122	2.90	12.0	36.0	2817	1.42	11.1	41.9
295	2.84	(9.0)	42.2	3191	1.34	10.1	40.4
464	2.54	(15.5)	48.7	3327	1.24	11.2	43.4
1489	2.00	12.0	39.3	4260	1.00	11.2	44.7
1651	1.94	11.4	36.3	4614	0.95	10.8	43.6

Mean, $K_{mol.} = 0.00026$. Mean, $K_{OH} = 40.7$.

Table XLI.

$V = 125$.				$w = 50$ cc.			
t.	vt.	43430 $K_{mol.}$	K_{OH}.	t.	vt.	43430 $K_{mol.}$	K_{OH}.
0	4.00	....	....	1780	2.57	10.8	44.7
202	3.77	11.0	47.6	2793	2.09	10.1	44.0
437	3.67	(8.5)	(32.25)	3165	1.91	10.1	44.9
1460	2.90	9.0	38.3	3301	1.85	10.1	45.6
1653	2.67	10.1	43.4	4233	1.49	10.1	48.3
				4586	1.35	10.2	50.4

Mean, $K_{mol.} = 0.00024$. Mean, $K_{OH} = 45.2$.

It will be seen that $K_{mol.}$ does not vary with V, its average being 0.00026.[1] The relation existing between V and K_{OH} as well as between this K_{OH} and the K_{OH} determined from the velocity in strongly alkaline solutions, has been fully discussed.

The experimental data of this investigation have justified us in certain definite conclusions, which shall be briefly stated here:

[1] Derby found 0.00028.

I. The speed of the decomposition of the imidoester salts by water is dependent on their positive ions as is shown in Part I. The velocity is proportional to the concentration of the ions, but is also influenced by a "salt effect," which is due to the imidoester salt itself. We have here, in other words, an "auto-salt effect." The reaction is represented by the equation

$$RC(:\overset{+}{N}H_2)OR' + H_2O = RCOOR' + \overset{+}{N}H_4.$$

II. The imidoesters are amphoteric in character; the negative ions decompose into nitriles and alcohol (ions) with a velocity proportional to their concentration. Since the acid ionization is very slight, the concentration of negative ions is proportional to that of the ester and that of the hydroxyl ions, and therefore the action has the appearance of a so-called "catalytic" action of hydroxyl on the molecular ester. The reaction is represented by the equation

$$RC(:\overline{N})OR' = RCN + \overline{O}R'.$$

III. The nonionized molecules appear to decompose also into nitriles and alcohols with a much smaller velocity than that exhibited by the negative ions. The reaction is given by the equation

$$RC(:NH)OR' = RCN + HOR.$$

In conclusion, the writer takes pleasure in acknowledging gratefully his appreciation of Dr. Stieglitz's suggestive guidance of his work, and of the interest he has taken in it.

THE DECOMPOSITION OF CERTAIN MINERALS AND INDUSTRIAL PRODUCTS BY MEANS OF SODIUM PEROXIDE AND METALLIC SULPHIDES.

By James H. Walton, Jr., and Herman A. Scholz.

In the year 1893 J. Clark[1] published a method for decomposing pyrites, zinc blende, galena, chromium, and arsenic ores

[1] J. Chem. Soc., **63**, 1079–1083 (1893).

by mixing them with sodium peroxide in an open platinum or nickel dish and fusing in the usual manner. W. Hempel[1] used a similar method for the decomposition of chromium, manganese, tungsten, and titanium ores. Spüller and Kalman,[2] Edinger,[3] Saniter,[4] Glaser,[5] Angenot,[6] and Lucchese[7] used sodium peroxide for the decomposition of various organic and inorganic substances. These investigators all followed the method of placing the substance to be decomposed in a crucible, mixing with sodium peroxide, and applying heat to the crucible. While the decompositions made in this way are very complete, the sodium peroxide attacks the crucible vigorously, and a large amount of foreign matter is consequently introduced into the determination.

A number of investigators have published methods of decomposition in which the heat necessary to bring about the decomposition is furnished by the reaction between the peroxide and some organic substance present in the mixture. S. W. Parr[8] decomposed coal by mixing it in a steel bomb with sodium peroxide and igniting the mixture by dropping a red-hot iron wire into the mass, the combustion taking place without further application of heat. Although this method was used primarily for the determination of the heating power of coals, it was found that the sulphur was completely oxidized to the sulphate and could be determined in the usual manner.

Pringsheim[9] used a similar method for the quantitative and qualitative determination of the halogens, arsenic, and phosphorus in organic compounds. Von Konek[10] also used this method for making qualitative analyses of organic substances, using a cylindrical nickel or steel crucible similar to

[1] Z. anorg. Chem., **3**, 193–194 (1893).
[2] Chem. Ztg., **17**, 881, 1207, 1360, 1412 (1892); **18**, 292 (1893).
[3] Z. anal. Chem., **34**, 362–368 (1895).
[4] Chem. Ztg., **19**, 1657 (1898).
[5] J. Am. Chem. Soc., **20**, 130–133 (1898).
[6] Z. ang. Chem., **17**, 1274 (1904).
[7] Ann. chim. anal. appl., **9**, 450 (1905).
[8] J. Am. Chem. Soc., **22**, 646 (1900).
[9] This Journal, **31**, 386 (1903); Ber. d. chem. Ges., **37**, 2155 (1904); **38**, 2436 (1906).
[10] Z. ang. Chem., **17**, 771, 1093 (1904).

that designed by Parr for use in his calorimeter. The finely powdered sample, in this case, was mixed with sodium peroxide and a compound rich in carbon, such as camphor, and the mass ignited by dropping in a red-hot iron wire.

The decomposition of substances by means of the heat obtained from the action of the sodium peroxide on an organic compound mixed with the substance has several advantages. In the first place, the vessel in which the decomposition is carried out is attacked to an extent which is for many purposes inappreciable. Moreover, the decomposition is completed in a very few minutes. It seemed to the authors that this method could be modified and used to decompose certain substances of technical importance, particularly those which require the use of nitric acid for their decomposition, the excess of which must often be removed by evaporation with sulphuric acid before the determination can be made.

EXPERIMENTAL.

The sodium peroxide used in these experiments was the ordinary commercial article manufactured by Koenig & Co. It contained traces of SiO_2, Al_2O_3, and Fe_2O_3. Its purity was determined by measuring the volume of oxygen which was given off from a weighed amount of the substance when decomposed by water containing a few drops of a dilute solution of cobalt nitrate.[1]

The sample used in this work contained between 95 and 96 per cent sodium peroxide.

The Decomposition of Substances containing Lead.

a. Galena Ores.—Two galena ores were used in testing this method of decomposition. The percentage of lead present was first determined gravimetrically by boiling the finely ground ore (passed through a 200-mesh sieve) with concentrated nitric acid and a small amount of hydrochloric acid for one and a half hours, precipitating the lead as the sulphate, filtering, separating the lead sulphate from the residue by dissolving in hot ammonium acetate solution, reprecipitating

[1] Archbutt: Analyst, **20**, 3 (1895).

by means of sulphuric acid, and weighing the lead sulphate on a Gooch crucible.

The following values were obtained:

	Per cent of lead.	
	1.	2.
Ore No. 5	61.58	61.52
Ore No. 22	56.05	55.98

These iron ores contained a small amount of iron pyrites and a little silica. Long boiling with acid was found to be absolutely necessary to completely decompose them. In one case in which the ore was boiled for only one-half hour, results were obtained which were several per cent lower than those given above. The above results were taken as the true values for these ores as they agree with analyses made later by different methods.

For the purpose of determining the right kind of sodium peroxide mixture to decompose these ores, a number of qualitative experiments were made in which the ores were placed in the bomb of a Parr calorimeter and mixed with sodium peroxide and various easily oxidizable substances such as magnesium, ammonium oxalate, and starch. The thoroughly mixed charge was ignited by dropping a red-hot piece of iron wire into the water-cooled bomb. When starch was used the mass fused quietly. It was found that the addition of a small amount of potassium persulphate to the sodium peroxide gave a better fusion and an apparently complete decomposition of the ore.[1]

The following quantitative experiment was carried out:

Experiment 1.

0.3 gram ore No. 5 (200-mesh sieve).
5.0 grams sodium peroxide.
0.2 gram starch.
0.3 gram potassium persulphate.

This mixture was ignited in a closed bomb by means of a fine iron wire which passed through the charge, and which was heated to a red heat by means of an electric current.

[1] S. W. Parr: J. Am. Chem. Soc., **24**, 167 (1902).

The melt was dissolved in 100 cc. of water and enough sulphuric acid added to neutralize the alkali and leave an excess of 2 per cent acid. Sodium bisulphite was added to reduce the lead peroxide and the solution was boiled for five minutes. It was then diluted and the lead determined gravimetrically as the sulphate.

The following results were obtained:

	Per cent of lead.		
Ore No. 5	57.49	60.22	59.13

In these experiments it was observed that the fusion did not take place quietly, but was attended by slight explosions, which threw the fused mass upon the side of the bomb. It seemed reasonable to believe that this fact might be the cause of the low results.

Zinc sulphide, when mixed with sodium peroxide and ignited, is oxidized with the evolution of great heat, the oxidation taking place quietly, however. The following quantitative experiment was made in which this substance was substituted for the starch. The zinc sulphide used was the dry, finely divided product prepared by Kahlbaum.

Experiment 2.

0.5 gram ore.
8.0 grams sodium peroxide.
0.8 gram zinc sulphide.
0.3 gram potassium persulphate.

The mixture was placed in an open bomb and ignited as before. The entire mass became liquid and red-hot, and the fusion took place without any spattering. The following results were obtained:

	Per cent of lead.	
	1.	2.
Ore No. 5	60.61	59.73
Ore No. 22	55.51	55.18

In this series the lead sulphate was determined by titrating the ammonium acetate solution of lead sulphate with ammo-

nium molybdate according to Alexander's method,[1] the melted mass from the fusion being treated in other respects as in Experiment 1. The results obtained in the analysis of the two ores are somewhat better than those obtained when starch was used, but they are from 0.5 to 1.00 per cent lower than the values obtained by the acid decomposition method.

In several cases in which the above charge was used the decomposition was found to be incomplete, a slight amount of the ore remaining undecomposed in the sharp edge of the bomb at the point at which the wall and bottom intersect. It was apparent that this part of the bomb did not become sufficiently hot to decompose the ore. Since the fusion takes place quietly, it was found possible to avoid this uncertainty of decomposition by using a nickel crucible which has rounded edges and consequently affords no place for the ore to lodge. Moreover, the melt could be more easily removed and less water was needed for its solution. The nickel crucible used had a capacity of 30 cc. and was $1\,^{5}/_{8}$ inches in diameter. The charge was placed into the crucible and ignited by means of a short piece of magnesium ribbon instead of iron wire, which caused considerable trouble by forming the magnetic oxide of iron. This compound, being difficultly soluble, remains as a residue and makes it very difficult to tell whether or not the ore is completely decomposed.

Experiment 3.—The charge used was the same as in Experiment 2. The dry, finely ground sodium peroxide was measured by means of a small aluminum scoop. The other substances were added and thoroughly mixed by means of a glass rod, which was then brushed clean. The cover was placed upon the crucible and was moved far enough to one side to permit the dropping in of a piece of lighted magnesium ribbon about one-half inch in length.

After the ignition had taken place the crucible was immediately covered. The lead was determined by the molybdate method, the following results being obtained:

[1] Alexander: Eng. and Min. J., **13**, 55. See also Bull. School of Mines Quarterly **23**, 348 (1902).

	Per cent of lead.	
	1.	2.
Ore No. 5	61.23	61.22
Ore No. 5 (gravimetrically)	60.68	59.07
Ore No. 22	55.82	55.68

These low results might be due to incomplete decomposition, although, from the fact that no residue could be seen on dissolving the fusion in acid, this seemed improbable. To test this point, however, a sample of the ore was fused with sodium peroxide in an iron crucible, the heat being supplied by a Bunsen burner.

Experiment 4.

0.3 gram ore No. 5
5.0 grams sodium peroxide.

This mass was kept in a molten condition for five minutes and the lead determined gravimetrically. The results were low, 60.07 and 60.06 per cent of lead being found in duplicate determinations.

It will be seen that the results obtained with ore No. 5, in Experiments 2, 3, and 4, vary between 59.07 and 61.23. It was noticed that in the experiments in which the lowest results were obtained the precipitate of lead sulphate was colored dark brown, due to basic sulphates of iron which are precipitated upon boiling in a slightly acid solution when large quantities of alkali salts are present.[1] It occurred to the authors that these basic iron salts kept the lead sulphate from being dissolved by the ammonium acetate solution, the effect being similar to that produced by the presence of barium sulphate.[2]

To test this idea the following experiments were carried out:

Experiment 5.—A fusion of ore No. 5 was made as in Experiment 3 and the melt treated as before, except that the boiling on acidifying was omitted in order to prevent, as much as possible, the formation of the basic iron salts. The solution was heated to the boiling point and then allowed to cool. The residue still had a brown color, but it was much lighter

[1] Pickering: J. Chem. Soc., **37**, 807 (1880).
[2] Bull. School of Mines Quarterly, **23**, 348 (1902).

than before. The lead was determined by the molybdate method, the percentages found being 61.23 and 61.16.

Experiment 6.—This fusion was also carried out as in Experiment 3. The crucible and melt were put into a casserole and about 75 cc. of water containing 7 cc. of sulphuric acid (sp. gr. 1.84) were added. Enough sulphuric acid was present to neutralize all of the alkali. The melt dissolved in two of three minutes and the crucible was immediately removed. An excess of 4 cc. of sulphuric acid (sp. gr. 1.40) was then added, and a concentrated solution of sodium bisulphite poured in to reduce the lead peroxide. The solution was boiled for a minute, diluted to 200 cc., cooled, and 20 cc. of 95 per cent alcohol added. The residue was almost pure white. The lead was determined by the molybdate method, 61.46 per cent being found present. On repeating the determination, following the procedure described, the values 61.51 and 61.57 per cent were obtained.

Ore No. 22 was analyzed by the same method, 55.89 and 55.88 per cent of lead being obtained. These results agree closely with those obtained by the acid decomposition method. It seems logical to conclude that the low results were due to the presence of the basic salts of iron. The formation of these basic salts may be avoided by dissolving the fusion in acidified water.

In order to determine the value of the above method of decomposition as a general method for the decomposition of other substances containing lead, experiments were carried out in which some typical substances were analyzed by the sodium peroxide method, and also by the standard method.

Experiment 7.—A low grade galena ore (No. 45), high in both silica and iron pyrites, was decomposed by boiling with nitric and hydrochloric acids, and the lead determined gravimetrically, 3.13 per cent lead being found. The ore was also decomposed by means of the following charge:

1.00 gram ore No. 45 (through 200-mesh sieve).
10 grams sodium peroxide.
0.8 gram zinc sulphide.
0.3 gram potassium persulphate.

The mixture was ignited by means of a magnesium ribbon. A very hot fusion was obtained, due to the oxidation of the pyrite in the sample. The melt was treated as in Experiment 6 and the lead determined by titration with ammonium molybdate solution, the values 3.16 and 3.19 per cent of lead being obtained in duplicate determinations.

b. Lead Glaze.—A lead glaze high in calcium and silica was analyzed by the two methods. A one gram sample of the glaze (200-mesh sieve) was decomposed by the nitric acid method and the lead determined by the molybdate method. The large amount of silica caused difficulties both in filtering the insoluble residue and in dissolving the lead sulphate in ammonium acetate solution, necessitating a much longer boiling.

	1.	2.
Per cent of lead in glaze	27.81	27.82

Experiment 8.

1.0 gram glaze (200-mesh sieve).
10.0 grams sodium peroxide.
1.5 grams zinc sulphide.
0.4 gram potassium persulphate.

Since there was no combustible matter in the sample, it was necessary to raise the proportion of zinc sulphide. The fusion was good and the glaze completely decomposed. The melt dissolved in water, the absence of iron making unnecessary the precautions taken in the previous analyses to avoid the precipitation of basic salts. The lead determined by the molybdate method gave 27.84 and 27.82 per cent lead. In this fusion the silica went into solution almost completely and was filtered off from the insoluble residue and thus did not interfere in the filtering nor in the solution of the lead sulphate.

c. Lead Slag.—A sample of 0.5 gram of lead slag (100-mesh sieve) was decomposed by nitric and hydrochloric acids and the lead determined by the molybdate method, 36.39 per cent being found.

Experiment 9.

0.5 gram lead slag (100-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited with magnesium wire. The fusion was good and the decomposition appeared to be complete. Since there was very little iron present, the melt was dissolved in water and treated in the usual manner and the lead determined by the molybdate method. Results were 36.58 and 36.48 per cent lead.

These results by the sodium peroxide method compare very favorably with those obtained by the standard nitric and hydrochloric acid decompositions, as may be better seen from Table I.

Table I.—Comparison of Lead Determinations by Standard and by Sodium Peroxide Methods of Decomposition.

Sample.	Standard method, per cent Pb.	Peroxide method, per cent Pb.
Galena ore No. 5	61.58[1]	61.46
" " " 5	61.62[1]	61.51
" " " 5	...	61.57
" " " 22	56.04[1]	55.89
" " " 22	55.98[1]	55.90
" " " 22	...	55.88
" " " 45	3.13[1]	3.16
" " " 45	...	3.19
Lead glaze	27.81	27.84
" "	27.82	27.88
" slag	36.39	36.48
" "	...	36.58

Sodium Peroxide Method of Decomposition Applied to Manganese Determinations.

Since the sodium peroxide and zinc sulphide mixtures were so effective as fluxes in the lead determinations, they were tried on manganese compound.

a. Analysis of Manganese Glaze.—A manganese glaze high in silica, but containing no calcium, was first used. It was not attacked to any appreciable extent by nitric and hydrochloric acids, even after boiling for an hour. One gram of the glaze (200-mesh sieve) was fused with sodium carbonate in a platinum crucible. The melt was dissolved, made acid

[1] Lead determined gravimetrically as $PbSO_4$.

with sulphuric acid (sp. gr. 1.42), and the manganese determined by Volhard's[1] method.

	1.	2.
Per cent of MnO in the sample:	4.57	4.55

Experiment 10.

1.0 gram manganese glaze (200-mesh sieve).
1.4 grams zinc sulphide.
1.0 gram sodium peroxide.
0.4 gram potassium persulphate.

Ignited in a nickel crucible by means of magnesium ribbon. Very good fusion and apparently complete decomposition, for no residue was left on acidifying with sulphuric acid and adding a little sodium sulphite. The melt was dissolved in water, acidified with sulphuric acid (sp. gr. 1.42), and sodium bisulphite was added to reduce manganese dioxide. The sulphur dioxide was boiled off and the manganese determined by Volhard's method. Results: 4.57 and 4.55 per cent MnO.

b. Analysis of Franklinite.—The sample of franklinite contained considerable silica. As is well known, it is a very refractory mineral which cannot easily be decomposed by sodium carbonate fusion, is decomposed with great difficulty by potassium bisulphate fusion, and is decomposed by concentrated nitric and hydrochloric acids only after long boiling. A one gram sample (200-mesh sieve) was boiled for two hours with nitric acid (sp. gr. 1.42) containing a small quantity of hydrochloric acid (sp. gr. 1.12). Ten cc. sulphuric acid were added and the solution boiled down to sulphuric acid fumes. It was diluted and the manganese determined by Volhard's method. Results were: 7.89 and 7.96 per cent MnO.

Experiment 11.

1.0 gram franklinite (200-mesh sieve).
8.0 gram sodium peroxide.
1.2 grams zinc sulphide.
0.4 gram potassium persulphate.

Ignited by magnesium in a nickel crucible. The mixture became liquid and red-hot but the decomposition was not complete.

[1] Volhard: Ann. Chem. (Liebig), **198**, 318.

The proportions of the components were varied but it was impossible to get a complete decomposition with these ingredients. It was therefore decided to substitute for the zinc sulphide some substance which would give more heat. Iron pyrites and a small amount of magnesium powder were found to answer this requirement very well.

Experiment 12.

1.0 gram franklinite (200-mesh sieve).
8.0 grams sodium peroxide.
0.3 gram powdered magnesium.
0.3 gram potassium persulphate.
2.0 grams pyrite.

Ignited by magnesium wire in a nickel crucible. The fused mass was extremely hot and remained liquid and red-hot for about two minutes. It gave a complete decomposition of the franklinite, but the melt dissolved very slowly, in about two hours. This was remedied by sifting 3 to 4 grams of sodium peroxide into the liquid mass and gently rotating the crucible to mix the peroxide with the molten mass. The contents of the crucible, after cooling, dissolved easily in water in 3 to 4 minutes. The solution was made acid with sulphuric acid (sp. gr. 1.42), the manganese dioxide reduced by sodium bisulphite, and the manganese determined by Volhard's method as in the other determination.

	1.	2.
Percentage of MnO	7.90	7.88

c. Analysis of Ferro-manganese.—A 0.5 gram sample of ferro-manganese which had been passed through a 100-mesh sieve was dissolved by boiling for about an hour in nitric acid (sp. gr. 1.42). Sulphuric acid was added and the solution was evaporated to sulphuric acid fumes. The manganese was determined by Volhard's method as in the franklinite determinations. Results were 56.25 and 56.23 per cent manganese.

Experiment 13.

0.5 gram ferro-manganese (100-mesh sieve).
8.0 grams sodium peroxide.
0.8 gram zinc sulphate.
0.3 gram potassium persulphate.

Ignited by means of magnesium ribbon. A red-hot liquid mass was obtained, and the substance apparently decomposed completely. The melt dissolved with difficulty. Three to four grams of sodium peroxide sprinkled into the fused mass produced a melt that was dissolved easily in a few minutes. The solution was acidified with sulphuric acid, the manganese dioxide reduced with sodium bisulphite, and the manganese determined by Volhard's method as before. Results: 56.18 and 56.32 per cent manganese.

Table II.—Comparison of Standard and Sodium Peroxide Methods of Decomposition for Manganese Determinations.

Sample.	Standard method, per cent MnO.	Peroxide method, per cent MnO.
Manganese glaze	4.57	4.58
" "	4.55	4.55
Franklinite	7.89	7.90
"	7.96	7.88
	Per cent Mn.	Per cent Mn.
Ferro-manganese	56.25	56.18
"	56.23	56.32

The manganese in each case was determined by Volhard's method.

The Decomposition of Chrome Iron Ore.

For these experiments a chrome iron ore high in chromium was used. It was first analyzed by fusing in a porcelain crucible with sodium peroxide, dissolving the fused mass in water, and destroying the excess of the peroxide by boiling. To the dichromate solution an excess of standard ferrous sulphate solution was added and the excess above that necessary to reduce the sodium dichromate was determined by titrating with standard potassium dichromate. The results obtained were 47.09 and 47.12 per cent Cr_2O_3.

Experiments with a charge similar to that used in Experiment 11 showed that not enough heat is obtained with the zinc sulphide to completely decompose the chrome iron ore.

A mixture of pyrite and magnesium was found to work satisfactorily.

Experiment 14.

0.5 gram chrome iron ore (through 200-mesh sieve).
8.0 grams sodium peroxide.
0.3 gram potassium persulphate.
2.0 grams iron pyrites.
0.3 gram magnesium.

Ignited in the usual manner. The fusion was very hot, but it was necessary to sift 3–4 grams of sodium peroxide in the liquid mass to make it dissolve easily. The chromium was determined volumetrically, 47.07 per cent being found in the sample.

The Application of the Sodium Peroxide Method of Decomposition to Silica Determinations.

In order to investigate the adaptability of the sodium peroxide method to silica determinations, a blast furnace slag was decomposed by this method and by the standard method and the percentages of silica obtained by the two methods compared. For the standard method 1.0 gram of the slag (200-mesh sieve) was boiled for an hour with hydrochloric acid (sp. gr. 1.12). The slag appeared to be completely decomposed. It was evaporated to dryness on the water bath and kept there for several hours after it was dry. It was moistened with hydrochloric acid, dissolved in water, and the silica filtered off. The filtrate was dehydrated a second time. The silica was ignited to constant weight in a platinum crucible and then volatilized in the usual manner, the silica being determined by difference. The results obtained were 30.06 and 30.04 per cent SiO_2.

Experiment 15.

0.5 gram slag (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited the above mixture by means of magnesium ribbon in a nickel crucible. A good fusion was obtained. The melt

dissolved easily in water and no residue was left on acidifying with hydrochloric acid. The silica was dehydrated twice and determined as before. The results were 30.02 and 29.98, as against 30.04 and 30.06 per cent by the standard method.

Qualitative Experiments.

Qualitative experiments were carried out in order to test the adaptability of this method to the decomposition of various substances.

a. Monazite.—The sodium peroxide method of fusion was tried on a sample of monazite containing 2.75 per cent ThO_2.

Experiment 16.

1.0 gram monazite (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited the above mixture with magnesium ribbon. The decomposition was complete, for upon acidifying with hydrochloric acid no residue was left.

b. Clays.—A brick clay of the following composition was used: SiO_2, 60.93; Al_2O_3, 17.93; Fe_2O_3, 8.12; MgO, 0.91; CaO, 1.35; Na_2O and K_2O, 5.01; volatile matter, 5.73 per cent.[1]

Experiment 17.

1.0 gram clay (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

It was ignited by means of a magnesium ribbon. The fusion was quiet. The fused mass dissolved completely in hydrochloric acid, leaving no residue.

Experiments were made with a fire clay of the following composition: SiO_2, 67.37; Al_2O_3, 21.69; Fe_2O_3, 1.59; TiO_2, 1.32; loss on ignition, 8.70 per cent.

Experiment 18.

1.0 gram fire clay (200-mesh sieve).
8.0 grams sodium peroxide.
0.3 gram potassium persulphate.
1.2 grams zinc sulphide.

[1] This analysis and the one of the fire clay were made by the chemists of the Illinois State Geological Survey.

The above mixture was ignited by means of magnesium ribbon. The melt, when taken up in water and made acid with hydrochloric acid, went into solution completely, leaving no insoluble residue. This method may be used advantageously in connection with the determination of titanium by the method described by one of the authors.[1]

c. Copper Matte.—A copper matte high in copper was used in the following experiments:

Experiment 19.

1.0 gram copper matte (200-mesh sieve).
8.0 grams sodium peroxide.
0.5 gram zinc sulphide.
0.3 gram potassium persulphate.

This mixture was ignited in the usual manner. The mass became very hot and liquid. It was necessary to sift 3 to 4 grams of sodium peroxide into the molten mass to make it dissolve easily. The melt, when taken up in water and acidified with hydrochloric acid, dissolved completely, leaving no residue.

d. Bauxite.—A sample of bauxite containing a considerable amount of iron and titanium oxides was used for the following experiments:

Experiment 20.

0.5 gram bauxite (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited by means of magnesium ribbon. The fusion was good but the decomposition of the ore very poor. Consequently the pyrite mixture was tried.

Experiment 21.

0.5 gram bauxite.
8.0 grams sodium peroxide.
0.5 gram zinc sulphide.
1.0 gram pyrites.

[1] Walton: "The Colorimetric Determination of Titanium," J. Am. Chem. Soc., **29**, 481 (1907).

Ignited the above mixture by means of a magnesium ribbon. The fusion was extremely hot. Three or four grams of sodium peroxide were sifted into it to make the melt dissolve easily. The melt was dissolved in water acidified with hydrochloric acid. No residue was left, which indicated complete decomposition.

e. Titanium Iron Ore.—For a titanium iron ore, high in iron and titanium, a mixture essentially the same as that used in Experiment 20 was used, but it did not decompose 0.5 gram of the ore (200-mesh sieve).

A fusion of a mixture similar to that used in Experiment 21 completely decomposed 0.5 gram of the ore.

Notes and Precautions.

To ascertain the effect of the fusions on the nickel crucibles, two new crucibles were weighed, and after sixteen fusions had been made in each they were carefully cleaned and weighed again. The crucible weighing originally 18.7683 grams lost 0.2876 gram in 16 fusions. A crucible weighing originally 18.6119 grams lost 0.3363 gram in 16 fusions. This is an average loss in weight of about 0.02 gram for each fusion. When the hot oxidizing nature of the fusions is considered, this is a very slight loss. The fusions were those made with the lead ores, using sodium peroxide and zinc sulphide.

It was found that a piece of twine about an inch long, soaked in alcohol and lighted, can be used for igniting the mixtures instead of magnesium ribbon. This could be used if, for any reason, magnesium was not to be introduced into the mixture.

A finely divided sample was found to be necessary for the sodium peroxide fusions. In the foregoing experiments, with the exception of the ferro-manganese and the lead slag, it was found necessary to pass the substance to be analyzed through a 200-mesh sieve.

Since sodium peroxide often contains small lumps which keep the mixture from igniting or cause incomplete combustion, it is necessary to pulverize this substance before using it.

The different ingredients must be very thoroughly mixed. A partial mixing results in partial decomposition.

All the ingredients *must be perfectly dry.* The mixture is so easily ignited that if there is any moisture present it may react with the sodium peroxide and evolve enough heat to ignite the mixture prematurely.

Conclusion.

From the foregoing experiments it is evident that sodium peroxide, zinc sulphide, and potassium persulphate, when mixed in certain proportions, give a good fusion medium for the decomposition of the substances used in this investigation. In every case the new method gave results as good as those obtained by the standard method. With possibly slight modifications, it could be extended to numerous other substances, a few of which are indicated in the qualitative experiments. This method is particularly applicable to sulphide ores and to substances high in silica, such as glazes and slags. With basic substances, such as franklinite and chrome iron ore, it is necessary to use iron pyrites to get sufficient heat. Pyrite, however, cannot be used in a good many fusions where iron is objectionable, and to fusions of that nature this method cannot be applied.

The chief advantage of the method is the quickness with which decomposition can be accomplished. The entire operation, including mixing, igniting, cooling, and dissolving the melt, takes approximately five minutes. A decomposition by acid takes from half an hour to an hour and a half or even two hours. Moreover, in most cases the nitric or hydrochloric acid must be expelled by evaporating the solution down to sulphuric acid fumes, which necessitates considerable care and usually takes half an hour longer. In the sodium peroxide method sulphuric acid may be used directly for acidifying, which does away with the tedious evaporation.

In the new method the silica present is practically all brought into solution and kept there, so that it does not clog filters and cause other annoyances. The sulphur in sulphide ores and the carbonaceous matter in slags, etc., is easily and com-

pletely oxidized by the sodium peroxide method, and the laborious oxidation by means of nitric acid is avoided.

Another advantage arises from the fact that since these fusions are made in nickel crucibles, a saving is made in the amount of platinum ware used.

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ON THE THEORY OF INDICATORS AND THE REACTIONS OF PHTHALEINS AND THEIR SALTS.

BY S. F. ACREE AND E. A. SLAGLE.

[SECOND COMMUNICATION ON PHTHALEINS.][1]

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

Professor W. R. Orndorff has called our attention to the fact that he has obtained colored salts of trimethylgalleïn[2] and the corresponding tetrachlor derivative. Such substances as *p*-oxydiphenylphthalid,[3] the phenol methyl ester of phenolphthalein,[4] and the corresponding ethyl ester of tetrabromphenolphthaleïn[5] dissolve in alkalies without color.

Our theory of tautomeric salts takes account of these facts; since we did not discuss in detail this phase, and several others, in the first paper, we take this opportunity to present this point a little more minutely. We have found that the sodium salt of the phenol ethyl ester of fluoresceïn, apparently pure, dissolves in water with a color which, though very decided, is much less intense than that of fluoresceïn salts. Furthermore, this sodium salt dissolves in absolute methyl and ethyl alcohol, giving a very faint color at temperatures from —15° to 0° which increases very decidedly as the temperature is raised to 80°, but decreases again as the temperature is lowered. This sodium salt yields, on alkylation with ethyl iodide in 0.3 N solution of 40 per cent alcohol, at 60°, a mixture of the colorless phenol diethyl ester and the colored quinone diethyl ester.

[1] Acree: THIS JOURNAL, **39**, 528, 649; Stieglitz: *Ibid.*, **39**, 651.
[2] *Ibid.*, **26**, 97.
[3] Baeyer: Ann. Chem. (Liebig), **354**, 162.
[4] Ber. d. chem. Ges., **40**, 3728.
[5] *Ibid.*, **30**, 177.

Now the failure of some of these salts to give color and the appearance of color in others, as well as the formation of only one ester in some cases and of the two isomeric esters in other cases, is readily explained by our hypothesis. Using the phenol methyl ester of phenolphthalein as an example, we have the salts in the following tautomeric equilibrium, which varies widely with the different analogous compounds, just as do the tautomeric salts of the urazoles:[1]

$$(CH_3OC_6H_4)(NaOC_6H_4)C(OCOC_6H_4) \underset{}{\overset{}{\rightleftharpoons}} (CH_3OC_6H_4)(O:C_6H_4:)CC_6H_4COONa.$$
$$P \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad Q$$

In the case of this particular ester in the equation the salt seems to exist practically all as P and cannot form the *quinonephenolates* assumed by Stieglitz and by Acree; the solutions give no color and seem to yield only the phenol diester when heated with methyl iodide.[2] In the case of the colored sodium salt of the phenol ethyl ester of fluoresceïn, and of Professor Orndorff's trimethylgalleïn, etc., if these substances in hand are pure the equilibrium conditions must be different, and both P and Q must be present. Q gives color to the solution because (1) it has a quinone group and (2) it unites to a greater or lesser extent with P and forms an *intermolecular* quinonephenolate group. The same kind of evidence applies to the dibasic salts of phenolphthalein, fluoresceïn, etc., as was shown on pp. 541–544 of our first article. Mr. Slagle finds that P and Q yield the two corresponding esters when treated with alkyl halides. The tendency to form P and Q and the quinonephenolate groups will vary greatly with the different compounds; hence the apparent lack of color in some of the phenol esters of such compounds, as was discussed on p. 531, *et seq.*

Green and King[3] have explained this lack of color on the basis of the hydration of the quinone group:

$$(CH_3OC_6H_4)(HOC_6H_4)C(OCOC_6H_4) + \overset{+}{N}a\overset{-}{O}H \rightarrow (CH_3OC_6H_4)(HOC_6H_4)C(OH)C_6H_4\overset{-}{C}O\overset{+}{O}Na.$$

[1] Acree: THIS JOURNAL, **37**, 71; **38**, 1.
[2] Meyer and Spengler: Ber. d. chem. Ges., **38**, 1318.
[3] J. Chem. Soc., **85**, 398. Ber. d. chem. Ges., **40**, 3724

This, without doubt, plays an important part in some cases. But this point of view does not account, in the present case, for the formation of the nearly quantitative yields of the phenol dimethyl esters from methyl iodide and the sodium salts of phenolphthalein and hydroquinonephthalein, nor for the formation of *both* isomeric esters of fluoresceïn obtained by Mr. Slagle; our theory does account for these facts. It is unfortunate that no one has isolated these colorless salts and shown by analysis whether they are hydrated and become colored when dehydrated.

We must be very careful about drawing conclusions concerning the *colors* of these salts, as small amounts of salts of phenolphthalein, fluoresceïn, etc., often give rise to a great part or all of the color actually observed.

JOHNS HOPKINS UNIVERSITY,
April 15, 1908.

REPORT.

RECENT ADVANCES IN CHEMICAL INDUSTRY.

Methods of Combining Atmospheric Nitrogen.

Although the press has announced the discovery of new sodium nitrate deposits in Chili, the final exhaustion of all such deposits is but a question of years, and the problem of providing a cheap and sufficient supply of combined nitrogen is the chief chemical problem of the day.

Bacterial Action.—The work of the German factories and of the U. S. Department of Agriculture in distributing cultures of bacilli suitable for leguminous plants has not as yet proved as great a practical success as was hoped for. Possibly the cultures were not hardy enough. It seems certain, however, that the application of these cultures to seed or soil with favorable results will be a solved problem in the immediate future.

The recent work of Professor Bottomley, of King's College, London—if it should be confirmed by other workers—is most important. Bottomley claims to have developed new physiological varieties of the ordinary bacillus of leguminous plants which are capable of symbiosis with nonleguminous plants. As to his method, in one series of experiments he removed a colony of *bacillus radicicola* from the leguminous root and placed it in an infusion of tomato roots; the bacilli survived

this treatment and were bred for ten generations in the tomato root infusion, gradually learning to relish its flavor, so that when soil in which tomatoes were planted was sown with these bacilli, occasional nodules were formed on the tomato roots, with improvement of the crop from these plants. Bottomley adapted in the same manner *bac. radicicola* to cereals, roses, cabbages, and strawberries, and says that in every case root nodules were formed on some plants, with increased yield from these plants.

If this work is confirmed, and it proves possible in time to produce breeds of hardy bacilli which can be *relied* on to produce sufficient nodulizing for all plants, leguminous and non-leguminous, no nitrogenous fertilizers will be needed, and the nitrogen combination problem will be simplified.

Chemical Methods of Combining Atmospheric Nitrogen.

There are three general methods used technically; combining nitrogen with oxygen to yield nitrates or nitrites; nitrogen with carbon and calcium to yield calcium cyanamide; nitrogen with hydrogen to yield ammonia.

Nitrates.—The Birkeland-Eyde process, utilizing the thermal action of the arc on air in a magnetic field to form nitric oxide which is oxidized to nitrogen dioxide and this to nitric acid which is marketed as calcium nitrate, was fully described in THIS JOURNAL[1] at the time of its invention. As predicted, it has proved a practical success. Birkeland has obtained additional patents. The Badische Anilin- and Soda-Fabrik have patents bearing on this process and have established a partnership with the Birkeland-Eyde Company. The fact that a number of patents have been granted in Germany, France, and England on variations of this process, and on attempts to substitute for the magnetic field a mechanical spreading of the contact between arc and air, is further proof of a general belief in the success of the process.

Nitrites.—Nitric oxide in contact with air or oxygen forms nitrogen dioxide. Raschig[2] has, however, proved experimentally that nitrogen trioxide is formed as an intermediate product, and that the reaction velocity of the phase

$$4NO_2 + O_2 = 2N_2O_3$$

(15 seconds) is greater than that of the second phase,

$$2N_2O_3 + O_2 = 4NO_2$$

[1] THIS JOURNAL, **35**, 358.
[2] Z. ang. Chem., **1905**, 1281.

(60–80 seconds). The Badische Anilin- und Soda-Fabrik find that the second phase can be completely suppressed by keeping the gases at a temperature of about 300°, and have patented a process for making pure nitrites by keeping the gases which leave the Birkeland-Eyde furnace at this temperature, and passing them into solutions of bases which absorb the nitrogen trioxide.

Calcium Cyanamide.—The process of Frank and Caro has proved a commercial success. They conduct nitrogen (obtained by fractioning liquid air) over commercial calcium carbide heated from 750° to 1000° in an electric furnace; the nitrogen instantly reacts on the carbide which glows brightly, forming calcium cyanamide:

$$CaC_2 + N_2 = CN_2Ca + C.$$

Eleven cyanamide factories, with an annual capacity of 166,600 tons, are built or in process of construction in Europe. An "American Cyanamide Co." is building a plant with an annual capacity of 40,000 tons on the Tennessee river, in northern Alabama.

Cost of Combined Nitrogen.—P. A. Guye—who is an expert on this subject—in a lecture before the English Society of Chemical Industry,[1] said that the cost of combining nitrogen by the cyanamide process and by the Birkeland-Eyde process is about the same; he estimates it as about 24 cents per kilogram of nitrogen.

Ammonia from Generator Gas.—Although it is easy to obtain ammonia by the silent discharge in a mixture of pure nitrogen and hydrogen, Berthelot did not succeed in obtaining ammonia by the silent discharge in generator gas, but obtained polymers of formamide, $(HCONH_2)_n$. The Westdeutsche Thomas Werke,[2] however, have patented a process for obtaining ammonia from generator gas. By cooling the gas to 65° to 80° and using a current of 15,000 volts and 2 amperes, they change 20 per cent of the nitrogen in the generator gas into ammonia and market it as ammonium sulphate.

Ammonia and Electric Energy from Peat and from Fuel Waste.—Another method of obtaining ammonia which utilizes both the nitrogen of fuel and that of air and which many inventors are attempting to work out is illustrated in the process of Ward and Sugden,[3] in England, and of Frank and Caro[4] in Germany, for utilizing fuel refuse and peat.

[1] J. Soc. Chem. Ind., **1908**, 567.
[2] Chem. Ind., **30**, 552.
[3] Elek.-chem. Z., **14**, 84.
[4] *Ibid.*, **14**, 86; and Z. ang. Chem., **19**, 569.

It is realized that all processes based on utilizing peat as transportable fuel by compressing and drying it never have paid and cannot pay, as the volume of the peat is too great, even when compressed, as compared with its fuel value, to repay transportation, so that the consumption must be local. Of course, the idea of transforming the peat *in situ* into electric energy and transporting the energy to factories suitably placed suggested itself to many inventors. Frank and Caro have adopted Ludwig Mond's gas generator to a method for gasifying any kind of cheap fuel in a mixture of air and steam. They are using peat as dug from the bog, containing 50 per cent water, and also the refuse from the coal washers. The product is a fuel gas rich in ammonia. After removing the ammonia the gas is burned in large gas engines, generating power (gas engines of as much as 5000 horse power are used in Germany). Large plants for this process are in construction. It is stated that the yield in ammonia will pay the working expenses and the interest on the capital invested.

Ammonia from Coking Ovens.—Increased attention is now given to obtaining ammonia as a by-product of coking ovens. Indeed, the increased demand in Germany in 1906 for sulphuric acid to convert the ammonia into ammonium sulphate was so great that the domestic supply of acid was insufficient, and increased import was required.

Peat Paper.

Another use of peat is as raw material for wrapping paper and cardboard. An English syndicate working on an American patent has bought a large peat bog in Sweden for this purpose. It is said that the peat is converted into paper in two hours.

Graphite.

The output of artificial graphite by the International Graphite Co., of Niagara Falls, has steadily increased, being 5,074,757 pounds in 1906. Acheson, the inventor of carborundum and of artificial graphite, recently discovered a method of making very soft, pure graphite, and gave attention to utilizing it as a lubricant; he found that by treating the graphite with tannic acid it is changed from the flocculent form to so fine a powder that its emulsion in water passes readily through fine filter paper. He calls it "deflocculated" graphite, and its emulsions in water, in petroleum and in thin mineral oils have the properties of the best lubricators; one or the other of these emulsions forms a suitable lubricator for a given

type of machinery. The material is attracting attention here and abroad.

Silicon Monoxide.

Silicon monoxide,[1] SiO, is made by reducing silicon dioxide in the electric furnace by carborundum or carbon:

$$2SiO_2 + SiC = 3SiO + CO.$$

The material is a white solid, is patented under the trade-name "monox," and is used as an adjunct to paints.

Hydrogen.

The use of war balloons in Germany has led the German Government[2] to build works for making and storing hydrogen. The hydrogen is made by the Schuckert system by the electrolysis of a 20 per cent solution of potassium hydroxide at 60° to 70°. To prepare 1 cubic meter of hydrogen requires 6.4 kilowatts of energy. Iron anodes are used; 2 kilograms iron are used up per 100 cubic meters hydrogen. The gas is washed by scrubbers and passes to the gasometers used for filling the balloons, or is compressed in cylinders for storage. One establishment with a capacity for making 1200 cubic meters per 24 hours is completed; another is building.

Cellite.

Dr. Eichengrün, of Elberfeld, has invented a substitute for celluloid, which he calls cellite.[3] It is a cellulose acetate; it can be pressed and moulded like celluloid; is, in thin layers, as flexible as leather, somewhat elastic, transparent and clear, not acted on by water, and incombustible.

Artificial Silk.

The artificial silk manufacturers[4] have improved their product recently by employing a cellulose acetate, which gives a more durable fabric than that first marketed.

Sulphur.

The present position of the Louisiana and Italian sulphur industry in relation to the world's supply of sulphur is very interesting. As is generally known, the Louisiana sulphur is in a deep-lying bed, and is obtained by the Frasch process; superheated steam is forced through pipes into the bed, melt-

[1] Elek.-chem. u. metallurg. Ind., **1907**, 442.
[2] Elek.-chem. Z., **14**, 231 (1907).
[3] Chem. Ind., **30**, 476.
[4] *Ibid.*

ing the sulphur and forcing the molten sulphur to the surface in practically pure form. In round numbers, the Louisiana production in 1904 was 129,500 metric tons, in 1905 185,000, and in 1906 299,000. The production of Sicilian sulphur in 1905 was 569,000 metric tons, and in 1906 500,000.[1] It is estimated that the world's annual demand for sulphur (not including pyrite) is 500,000+ metric tons. The Louisiana deposit is estimated at 40,000,000 metric tons, and the possible production with the present plant is 3000 metric tons daily, or 900,000 yearly.[2] One hundred and fifty-six thousand metric tons of Sicilian sulphur were imported into the United States in 1893. The import shrunk to 41,000 metric tons in 1906.

The Anglo-Sicilian Co., which controlled the Sicilian sulphur production, not believing in the possibilities of the Frasch process, allowed 400,000 metric tons sulphur to accumulate, for which they could find no market; the company liquidated in August, 1906. To prevent the ruin of the Sicilian sulphur industry, which supports a great part of the population, the Italian Government has taken measures not only remarkable but unique in the relations of modern governments to industry.[3] The government bought the sulphur from the company for a price reported as $12.00 per metric ton, and made a law which unites the Sicilian mine owners to a compulsory syndicate, the "Consorzio obbligatorio per l' Industria Zolfifera." By the terms of this law a 50 per cent reduction of the former railroad freight on sulphur is granted, and only syndicate sulphur is allowed to be transported in or exported from Sicily at any price. In this way Italy hoped to meet American rivalry.

Not content with driving Sicilian sulphur from the American market, the Union Sulphur Co. (financed by the Standard Oil Co.) seems determined to monopolize the entire sulphur industry, and is offering American sulphur at Marseilles and Antwerp at $13.00 per metric ton, $20.00 being the average Marseilles price for Sicilian sulphur. American sulphur in New York costs $22.00 to $22.25, and is said by G. Lunge[4] to cost only $2.90 to the producers.

Foreign journals consider the situation very serious, and say that it is impossible for the Sicilian mines, which are surface workings, to compete against sulphur which can be mined by the Frasch process.

[1] Mineral Resources of U. S., **1906**, 1103.
[2] G. Lunge, in Z. ang. Chem., **1905**, 1009.
[3] Chem. Ind., **30**, 473 and 505 (1907).
[4] Z. ang. Chem., **1905**, 1009.

Steel.

In the manufacture of steel the increasing use of the electric furnace, particularly for making ferro-alloys and high-grade steels, is the point of greatest interest.

To understand the importance of these new steels it should be borne in mind that it is believed that there are three allotropic modifications of steel. It is assumed that there are three allotropic modifications of *iron*, α-, β-, γ-ferrites. Ordinary mild carbon steel is very soft at temperatures below 710° and is in the so-called α condition, in which the carbon is present as a carbide, Fe_3C (cementite), mixed with pure soft iron (α-ferrite). At temperatures between 710° and 810° the steel is in the β or martensite condition, very hard, the carbide going into solid solution in the β-ferrite. Above 810° the steel is in the γ, or austenite condition, in which the carbide is dissolved in γ-ferrite; it is moderately soft and extremely tough. These stages are reversed by slow cooling. If highly heated or molten steel is cooled suddenly or "chilled" it remains in the martensite or β condition at ordinary temperatures. If chilled steel is tempered, it is more or less changed at will in the direction of the α condition, and retains the desired properties at ordinary temperatures. But chilled steel is a supercooled solid solution, and both chilled and tempered steel are in a condition of unstable equilibrium which tends to revert through friction, heat, or jarring, to the normal α condition.

By alloying steel with one or more other elements—such as nickel, chromium, manganese, tungsten, etc., the transformation temperatures are lowered in proportion to the percentage of new element introduced, until the martensite or β form becomes that of stable equilibrium at ordinary temperature (self-hardening steel).

Such steel retains its hardness at temperatures much higher than ordinary steel, it does not lose its hardness ("temper") through frictional heat, and is used under the name of "high-speed" steel for tools. A steel containing 6 to 7 per cent chromium and either 20 to 25 per cent tungsten or 10 to 12 per cent molybdenum is a standard high-speed steel.

A still greater increase in the percentage of new metal makes the γ or austenite condition the stable one at ordinary temperature, forming exceedingly tough steel (automobile steels).

The electric furnace is exclusively used in making the ferro-alloys employed in steel making, such as ferro-silicon containing 25 to 90 per cent silicon; ferro-chrome, with 65 per

cent chromium; ferro-molybdenum with 80 per cent molybdenum; silico-manganese with 60 to 70 per cent manganese and 20 to 25 per cent silicon; and many others.

The use of various modifications of the Siemens-Martin open-hearth steel furnace, heated by the arc—each variety bearing the name of its inventor—is greatly increasing for the manufacture of high-grade steel; it is found that the high temperature of the furnace heated by the arc is required to obtain the best results with the β- and γ-steels. Under the general name "steel," alloys are now in use which we should have considered impossible a few years ago, such as the high-speed steels referred to above, or automobile steel containing 30 to 50 per cent nickel.

The study of the special properties imparted to steel by the addition of different amounts of each foreign element, or by addition of more than one foreign element, is most important; and the results already obtained are very interesting; but the subject is too detailed to be reviewed in a brief report.

E. RENOUF.

REVIEWS.

A HISTORY OF CHEMISTRY. By HUGO BAUER. Translation by R. V. STANFORD. New York: Longmans, Green & Co.; London: Edward Arnold. 1907. pp. 232. Price, $1.

This small volume will be of value to students of chemistry as an introduction to larger works on the history of chemistry. The history of a science cannot be treated in an elementary way, as it necessarily has to do with the most important advances in the subject. Only one who has a good knowledge of chemistry can follow the history of chemistry. Nevertheless, it is well for students in the early stages of their work to make an effort to learn what the important steps have been in the progress of their subject and to learn something about the leaders whose work has made the science what it now is. It is obvious that a beginner cannot, for example, make much out of a chapter dealing with the Theory of Nuclei and the Theory of Types, but he can read what is said of these subjects, and if he is rightly constituted he will keep at it, and some time the subject will clear up in his mind. To quote from the volume before us: "Recently the effort has also made itself felt to give life to the study of the history of chemistry by the publication of collections of important original researches, or of the correspondence of the earlier chemists. In this connexion the chief credit is due to W. Ostwald and

J. Kahlbaum. In the same way these pages, which can only present a short and incomplete course through the history of chemistry, may furnish an incitement to young chemists and students of chemistry to penetrate further into the origins and growth of chemical science."

The book can be heartily recommended for the purpose for which it was prepared. I. R.

KURZES LEHRBUCH DER ORGANISCHEN CHEMIE. Von WILLIAM A. NOYES. Mit Genehmigung des Verfassers ins Deutsche übertragen von WALTER OSTWALD und mit einer Vorrede von PROFESSOR WILHELM OSTWALD. Leipzig: Akademische Verslagsgesellschaft m. b. H. 1907. pp. 722.

A review of the original American edition of the book before us has already appeared in THIS JOURNAL. The author is to be congratulated on the appearance of this German edition prepared by Walter Ostwald, a son of the distinguished Professor Wilhelm Ostwald. The work of translation was probably undertaken at the instigation of Professor Ostwald, who has written an introduction in which he speaks in very complimentary terms of the book of Professor Noyes. His opinion can best be given in his own words: "Durch die eigenartige Anordnung des Stoffes ist es nun in der Tat möglich geworden, eine solche Symmetrie und Übersichtlichkeit des gesamten Materials herbeizuführen, dass der Student, welcher dieses kleine Buch kennen gelernt hat, seine weiteren Studien mit dem Vertrauen fortsetzen kann, dass er sich in dem Walde der organischen Chemie nicht mehr verirren wird. Dabei hat der Verfasser die unter solchen Umständen besonders schwierige Aufgabe gelöst, dem Schüler die Weite der von ihm künftig noch zu durchmessenden Gebiete zum Bewusstsein zu bringen, ohne ihm den Mut hierzu zu nehmen. Das Mittel hierzu ist die grosse Klarheit der Darstellung, welche den Schüler im gegebenen ganz zu Hause sich fühlen lässt, und ihm so das Vertrauen gibt, auch das Übrige noch bewältigen zu können." I. R.

DESCRIPTIVE BIOCHEMIE mit besonderer Berücksichtigung der chemischen Arbeitsmethoden. By SIGMUND FRÄNKEL. Wiesbaden: J. F. Bergmann. 1907. pp. 639. Price, M. 17.

The volume under consideration aims at fulfilling the functions of a "Beilstein" for biological chemists in which full descriptions of the various substances likely to be encountered will be found. In addition the book contains a mass of useful information concerning analytical and preparative methods and some account is given of the enzymes and the reactions

with which they are concerned. The value of a work of this character depends largely upon its completeness and upon the care taken in its compilation, and as a whole, the volume is deserving of high praise and indeed it has already won for itself a position among the most useful books in the biochemical laboratory.

Full references to the literature are furnished throughout and the author has taken the trouble to incorporate a considerable amount of work other than that of Teutonic origin. A glance at a volume of this kind would do much to convince the "pure chemist" of the fact that his physiological brethren are no longer content to work with "messes" and that an ever increasing portion of his work deals with definite substances capable of isolation in pure form.

Dr. Fränkel is to be congratulated on having produced a most admirable book.

H. D. DAKIN.

UNTERSUCHUNGEN ÜBER DIE GALVANISCHE LEITFÄHIGKEIT DER ELEKTROLYTE. Von SVANTE ARRHENIUS am 6 Juni, 1883, der kgl. schwedischen Akad. der Wissenschaften vorgelegte Abhandlung. Uebersetzt von ANNA HAMBURGER und herausgegeben von OTTO SACKUR. Mit 6 Figuren im Text. Leipzig: Verlag von Wilhelm Engelmann. 1907. pp. 153. Price, M. 2.50.

This epoch-making paper by Arrhenius is now translated into German and published as Ostwald's Klassiker der exakten Wissenschaften, Nr. 160. As is well known, this is one of the few great contributions which founded the modern science of physical chemistry. Physical chemistry has grown up from a few comprehensive generalizations: The Law of Mass Action; The Relation between Gas Pressure and Osmotic Pressure; The Theory of Electrolytic Dissociation; Faraday's Law as the Basis of Valence; and the Phase Rule.

This earlier work by Arrhenius was the forerunner of the theory of electrolytic dissociation, and it is now placed among the great classics of science where it undoubtedly belongs.

H. C. J.